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# **VARTM & RTM PROCESSING OF PBT & PA** **THERMOPLASTIC COMPOSITES.**

**FINAL REPORT TO OFFICE OF NAVAL RESEARCH,**  
**OCTOBER 2002.**

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## **Summary of Research**

Vacuum assisted resin transfer molding (VARTM) and resin transfer molding (RTM) processes have been successfully developed to enable infusion of thermoplastic pre-polymers into glass and carbon fiber performs at temperatures up to 210°C. The pre-polymers used in this study were CBT (Cyclic Butylene Teraphthalate oligomer) leading to a PBT composite, APLC-12 (Anionically-Polymerised Lactam -12) leading to a PA-12 composite, and APLC-6 (Anionically-Polymerised Lactam -6) leading to a PA-6 composite. Mixtures of PA-12 and PA-6 were also examined.

Traditionally it has not been easy to mold thermoplastic-reinforced composites due to their high viscosities. High temperatures and pressures were always required to fully impregnate fiber beds. Liquid composite molding processes, such as those demonstrated in this report, were virtually impossible. The employment of an activated pre-polymer melts eliminates the problems associated with high viscosity. All of the materials processed here were using vacuum pressure only.

For the CBT pre-polymer, a flat heated VARTM mold was used, together with a heated delivery system for transporting the molten resin from the melting unit to the mold. The fiber perform was bagged with a high temperature plastic film and sealing tape. The CBT pre-polymer (supplied by Cyclics Corporation), was melted by heating to 165°C. A catalyst was added just prior to infusion of the catalysed prepolymer into the fiber bed. The viscosity-time characteristics for this material, which polymerized within the mold to form polybutylene terephthalate (PBT), were measured to establish the VARTM processing window. Viscosity values for this material at 160°C varied from 0.1Pa.secs at introduction of the catalyst to 0.5Pa.secs

after approximately 60 minutes. This time was reduced to 16 minutes when the temperature was raised to 167.5°C.

Flat panels were successfully molded using S2 glass fabric, S2 glass mat, and carbon fabrics, with fiber volume fraction values over 45% achieved in the case of the glass, and up to 64% in the case of the carbon fabric. Comparison of DSC results between the PBT polymer and the PBT polymer within the composite indicated that the composition of the crystals was different in each case. DMA tests on the molded glass panels showed that the flexural storage modulus varied from approximately 18 GPa at room temperature to 9 GPa at 150°C for the S2 glass fabric/PBT composite. For the carbon fabric panels, flexural moduli up to 51 GPa were achieved, with flexural strengths of up to 450 MPa.

For the PA-12 and PA-6 pre-polymers, a rigid, electrically heated RTM mold was developed. A commercially-available anionic polymerization activator (Grinolit proved to be a quick, clean, and reliable method of producing un-reinforced polyamide 6, polyamide 12, and polyamide 6/12. Both the polymers and copolymers exhibited good mechanical strengths as well as good toughness and abrasion resistance. APLC 6 generally exhibited the highest tensile and flexural properties. APLC 12 generally exhibited the highest impact strengths.

The mechanical and physical properties of APLC 6/12 proved to be a compromise between APLC 6 and APLC 12. For the most part all of the properties of APLC 6/12 tested lay in between those of APLC 6 and APLC 12. Mechanical tests including tensile tests, flexural tests, and notched Izod impact tests, supported this statement. The melting temperatures of the co-polymers (evaluated by DSC) verified the compromise. Unusually, the copolymer actually had a higher rate of moisture absorption in two of the tests than either the PA-12 or PA-6.

The RTM system was used to infuse carbon-fabric reinforced PA-12, PA-6 and PA-6/12 composite plates. The PA-12 plates proved to have low void content, as was previously shown. The PA-6 plates, and all alloyed plates of PA-6/12 composites, however, tended to contain high void percentages when processed under vacuum conditions only. A compromise process was developed, using a heated press, and it was shown that application of up to 5 bar pressure, after vacuum infusion, could produce void-free laminates in the PA-6 and PA-6/12 laminates.

Extensive mechanical testing was carried out on the carbon-fabric reinforced laminates. In general, the PA-6 composites exhibited slightly higher compressive and flexural strengths than the PA-12 composites, whereas the PA-12 composites showed slightly higher tensile strengths, all of these properties being measured in the fiber direction. The properties of the PA-6/12 composites generally were generally lower than either the PA-12 or the PA-6 laminates, and in the case of the flexural moduli of the laminates, they were over 50% lower, due to high percentage void content.



**Section I – Development of an Elevated Temperature VARTM  
system for a cyclic PBT and glass fiber thermoplastic composite.**

**This work was carried out at the University of Delaware, during the period of  
August '01 to January '02.**

## **Development of an Elevated Temperature Vacuum Assisted Resin Transfer Molding system for Thermoplastic Composites**

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### **Abstract**

The vacuum assisted resin transfer molding (VARTM) process has been successfully developed to enable infusion of thermoplastic pre-polymers into a fiber perform at temperatures up to 180°C. A flat heated mold was used together with a heated delivery system for transporting the molten resin from the melting unit to the mold. The fiber perform was bagged with a high temperature plastic film and sealing tape. A 1-D heat transfer analysis predicted a 40°C temperature drop from the mold surface to the top surface of the fiber perform. An insulating layer placed on top of the preform reduced the temperature drop across the preform to an acceptable value of 10°C. The prepolymer used was a cyclic butylene terephthalate oligomer (supplied by Cyclics Corporation), which was melted by heating to 165°C. A catalyst was added just prior to infusion of the catalysed prepolymer into the fiber bed. The viscosity-time characteristics for this material, which polymerized within the mold to form polybutylene terephthalate (PBT), were measured to establish the VARTM processing window. Viscosity values for this material at 160°C varied from

0.1Pa.secs at introduction of the catalyst to 0.5Pa.secs after approximately 60 minutes. This time was reduced to 16 minutes when the temperature was raised to 167.5°C. Flat panels were successfully molded using S2 glass fabric and S2 glass mat with fiber volume fraction values over 45% achieved. DMA tests on the molded panels showed that the flexural storage modulus varied from approximately 18 GPa at room temperature to 9 GPa at 150°C for the S2 glass fabric/PBT composite.

**Keywords:** Thermoplastic composite, Elevated temperature VARTM

## 1.0 Introduction

The vacuum assisted resin transfer molding (VARTM) process has been developed from the more traditional resin transfer molding (RTM) process. In both processes a dry preform of reinforcing fibers is impregnated with a low viscosity resin followed by cure and de-molding. In the VARTM process, the preform is vacuum bagged on a one-sided mold as shown in Figure 1.1 and the resin is drawn into the preform under the negative pressure created by the vacuum. The use of a one-sided mold reduces tooling costs and other capital investment, which is a major advantage of the VARTM process. In Figure 1.1 the distribution media shown enables the resin to flow preferentially across the preform surface and simultaneously through the thickness<sup>1</sup>.

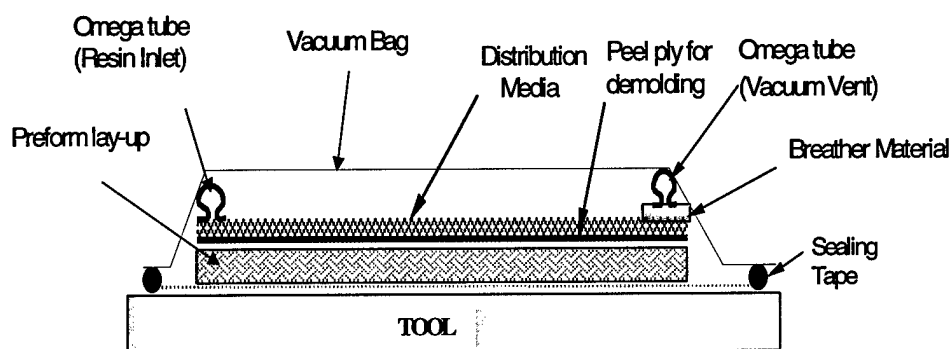


Figure 1.1 Traditional VARTM lay-up and tool arrangement

The Centre for Composite Materials (CCM) at the University of Delaware has been very active in developing room temperature VARTM, automating the process<sup>2,3</sup>, and modelling its flow behavior<sup>4</sup>. The VARTM process has proven to be a very efficient process for infusing low viscosity thermosetting resins into a fiber bed at room temperature. The composite can then be cured at a higher temperature as needed. In addition to the traditional method of VARTM processing of thermosetting materials at

room temperature, some high temperature thermosetting resins are being considered for processing using elevated temperature VARTM technology. However, VARTM at elevated temperature is still in the early stages of development as opposed to the classical RTM that is well established at high temperature<sup>5</sup>. An important issue for the successful development of elevated temperature VARTM is having a good understanding of the heat transfer from the mold through the fiber bed.

To characterize the thermal conductivity across a fiber bed, an easy and practical method was used in the research. This was based on measuring both the heat flow through the mold and the temperature drop across the fiber bed and recovering the thermal conductivity of the fiber bed from a simple 1-dimensional heat transfer analysis. Knowing thermal conductivity of the fiber bed enabled the determination of the temperature gradient across the preform together with the time and power required to heat up the preform to a specific temperature. Previous work<sup>6</sup> treated the preform as a mixture of solid fiber and polymer and the average thermal conductivity was theoretically estimated using rule of mixture by knowing two independent thermal conductivities for the fiber as a solid material and another for the polymer. The transverse effective thermal conductivity was also studied by Nig et al.<sup>7</sup>. Using an analytical model for different fabric weave, the same authors<sup>8</sup> also studied the in-plane effective thermal conductivity, where a micro mechanics model was developed based on a thermal-electrical analogy. This work characterizes the effective thermal conductivity based on experimental results, which gives the actual thermal conductivity that governs heat transfer and temperature gradient across the fiber bed.

In this research study an elevated temperature VARTM process was developed for infusing a molten, low viscosity, thermoplastic prepolymer into a fiber bed where polymerization took place at elevated temperature to form a thermoplastic composite part. Both the RTM and the VARTM processes have been made possible by the use of resins with viscosity values less than 1.0 Pa secs. Up until recently, viscosities in this range were only achievable with thermosetting resins, as the melt viscosity of most molten thermoplastics would be above 500 Pa.secs. This has traditionally rendered thermoplastics unsuitable for liquid molding. The reasons for wanting to use thermoplastics, is that they have many advantages over thermosets which include better impact resistance, are lighter, can be processed much faster, do not emit harmful volatiles during processing and can be easily recycled.

Within the past few years, research into potential methods for liquid molding of thermoplastics materials has resulted in the development of thermoplastics that can be molded in the prepolymer state. The resulting new generation of thermoplastics which have been developed for molding as prepolymers include Polyamides (PA-12, PA-6), Polybutylene terephthalate (PBT) and Polycarbonate. The molding viscosities of these new materials are in the region of 0.1Pa.secs. and consequently are poised to compete with thermoset materials through the processes of RTM and VARTM. The RTM process has been used successfully to mold a low viscosity pre-polymer form of a thermoplastic polyamide-12 material<sup>9</sup>. With this material, the monomer was melted at around 170<sup>0</sup>C, the activator added and infused into the preform, which was held at elevated temperature sufficiently long for the material to polymerize as a thermoplastic. More recently, the pre-polymer for PBT, Cyclic butylene terephthalate (CBT) has become available from the Cyclics Corporation in the USA.

The focus of this research has been to develop an elevated temperature VARTM process to mold cyclic butylene terephthalate (CBT), which with the addition of a catalyst, polymerized as a thermoplastic PBT. The molding of a PBT composite using the elevated temperature VARTM process is a new development, which required the thermal analysis of the process, the establishment of the process window for this material and the development of new processing apparatus.

## 2.0 Development of VARTM Process Window

### 2.1 Process window for PBT

The VARTM processing of thermoplastic composite parts from a catalysed prepolymer, means that the polymerisation process must take place within the mold in the presence of the fibers. The processing parameters have to satisfy the requirements for the satisfactory filling of the fiber bed together with the development of a fully polymerised matrix. The main factor which influenced the mold filling was the viscosity of the resin, which in turn was dependent on temperature, time and polymerisation rate. These characteristics were experimentally established for the PBT polymer and a suitable processing window defined such that the mold-filling phase of the VARTM process would be completed with a resin viscosity below 0.5Mpa.secs.

#### 2.1.1 PBT Material

PBT is an important matrix material in glass fiber reinforced composites, having attractive mechanical properties, good moldability and fast crystallization rate<sup>10</sup>. When used in composite applications, PBT has cost effective recycling advantages<sup>11,12</sup>. Physiochemical properties and morphology in PBT have been studied by various methods<sup>10,13-15</sup>. Thermal<sup>16,17</sup>, mechanical<sup>18</sup>, and electrical properties have also been reported<sup>19</sup>. The crystalline structure in PBT has been determined using different techniques such as X-rays, IR, Raman and NMR<sup>10,16-24</sup>. X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) were used to investigate the melting, reaction and crystallization behaviour<sup>11</sup>, which is a critical issue for the



molding of this material in its pre-polymer form. According to the company's (Cyclics) information<sup>26</sup>, the pre-polymer when mixed with the catalyst at temperatures above 155°C will undergo further polymerization, which will lead to a dramatic increase in viscosity. Consequently, the processing window (infusion time) for the elevated temperature VARTM process needs to be clearly defined to ensure that the infusion phase is complete while the viscosity is below 0.5 Pa.secs. The effects of time and temperature on the development of viscosity due to polymerization of the neat resin have been established using a rheometer. After the resin has been transferred into the fiber bed the polymerization and crystallization proceeds to completion.

#### 2.1.2 DSC measurements

To establish the melting and crystallization characteristics of the polymer, DSC experiments were conducted on both the pre-polymer and the polymer. The heating and cooling rate for all DSC experiments was set at 5°C per minute and the positive heat flow indicates an endothermic transition. The results are shown in Figure 2.1.

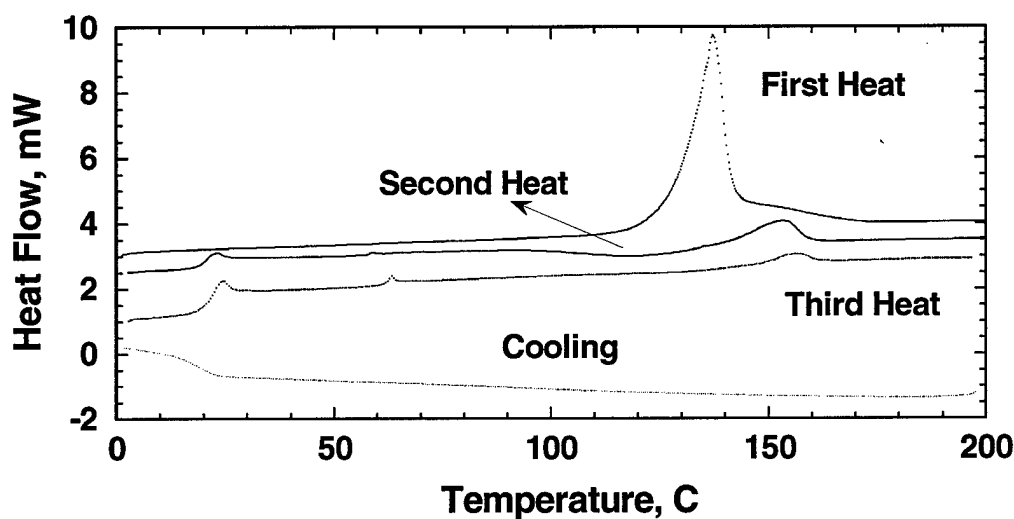


Figure 2.1: DSC of prepolymer

The sample was heated for three consecutive cycles. The first heat shows a relatively large melting peak at 137°C and no crystallization during cooling. On the second heating cycle, crystallization was followed by melting at 153°C. The third heating cycle indicated that the melting temperature rose to 156°C. From this information a minimum pre-polymer melting temperature of 160°C was chosen. When DSC measurements were carried out on the polymer (pre-polymer with 0.4% FASCAT 4101 catalyst), a crystallization peak was observed at 178°C during cooling, as shown in Figure 2.2.

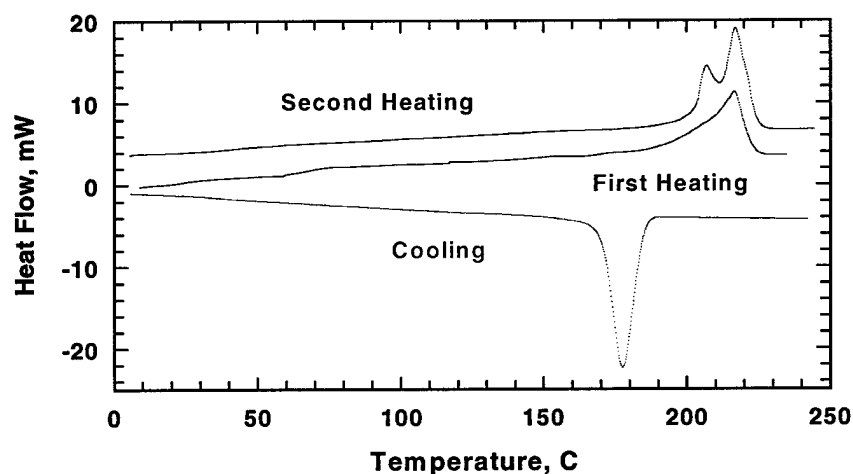


Figure 2.2 DSC of polymer

This information suggested that the temperature of the fiber pre-form, in which the resin polymerized and crystallized, should be above 178°C, which agrees with the material supplier's recommendation of 180°C.

### 2.1.3 Viscosity measurements

The successful filling of the fiber pre-form with the resin depended upon the viscosity of the resin remaining low for a sufficiently long period. To establish the process window for the viscosity, a series of viscosity measurements were carried out on both the pre-polymer and the catalysed pre-polymer with a parallel plate rheometer. The pre-polymer was melted in the rheometer at 180°C and the viscosity was measured continuously with temperature at 5°C per minute to 70°C. The results in Figure 2.3 show that the viscosity increased from 0.1Pa.sec at 180°C to 20Pa.sec at 70°C.

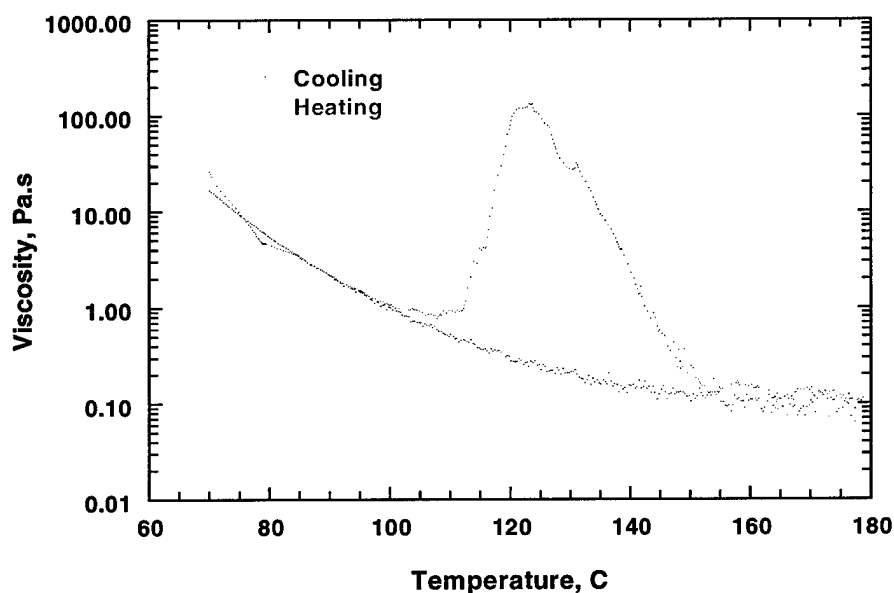


Figure 2.3 Viscosity values for PBT prepolymer

The sample was reheated at 5°C/min and it was found that the viscosity did not follow the cooling curve but instead showed a rise to 150Pa.sec between 110°C and 150°C. This rise would be consistent with the effects of crystallization starting at approximately 100°C as shown in the DSC results in Figure 2.1. As the reheating

continued from 150°C to 180°C the viscosity returned to the values of approximately 0.1Pa.sec recorded during cooling. The important observation for processing was that the pre-polymer could be heated and cooled between 130°C and 180°C while the viscosity remained within the range of 0.1Pa.sec to 0.2Pa.sec. Constant shear rate viscosity at three different temperatures (160°C, 167.5°C, and 175°C) was measured to establish the development of viscosity for the catalysed pre-polymer with time. The results of these tests are shown in Figure 2.4 and it can be seen that the viscosity strongly depends on temperature.

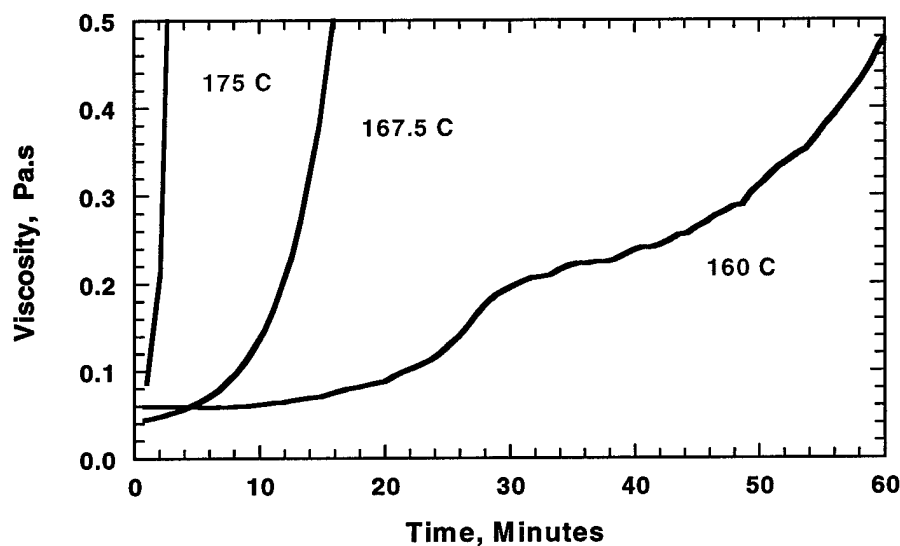


Figure 2.4 Viscosity values for PBT polymer

From the above results, the recommended process window for this PBT material is as follows:

- melt temperature for the pre-polymer and catalyst should be between 150°C and 160°C

- the pre-polymer should not be cooled below 130°C after the catalyst has been added
- the fiber pre-form should be heated to temperatures between 170°C and 190°C
- for a maximum viscosity of 0.5Pa.sec the infusion time would be between 60 minutes at a resin temperature of 160°C, and 16 minutes at a resin temperature of 167°C.

## 2.2 Thermal Analysis

In elevated temperature VARTM processing, the fiber preform was bagged and sealed on a flat heated metal mold. To achieve a suitable mold design, a heat transfer analyses was required to estimate the electrical power required to heat the mold and fiber perform to the processing temperature in a specified time. The metal plate and the fiber bed were treated as two layers of solid material with two different thermal properties. Transient heat transfer through a solid material in one direction is governed by:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (1)$$

where  $\alpha = \alpha_1$  for the metal plate and  $\alpha_2$  for the fiber-bed.

The interface between the two solid materials is governed by the amount of heat leaving first solid material block at the interface, which was equal to the amount of heat transferring into the second block of material (fiber bed) and is described by the following equation:

$$k_1 \left. \frac{dT}{dx} \right|_1 = k_2 \left. \frac{dT}{dx} \right|_2 \quad (2)$$

Also the temperature at the interface,  $T_m$ , is common for both solid materials.

This system doesn't have constant temperature boundary conditions since there was a heat source at one-side and heat losses at the other surface. Temperature was variable at both surfaces until the steady state condition is reached. For the transient period this system was solved numerically to give heating times and temperature gradients where the heat transfer properties of the materials were known. For this analysis an aluminum plate with a thermal conductivity of  $180 \text{ Watt/m}^0\text{K}$  was used together with a glass fiber bed. The thermal conductivity of the fiber bed was estimated using the rule of mixtures. The results of this analysis are shown in Figure 2.5 and from these the power requirement for heating a 12.5 mm thick aluminum mold to processing temperature was chosen as  $10 \text{ kW/m}^2$ .

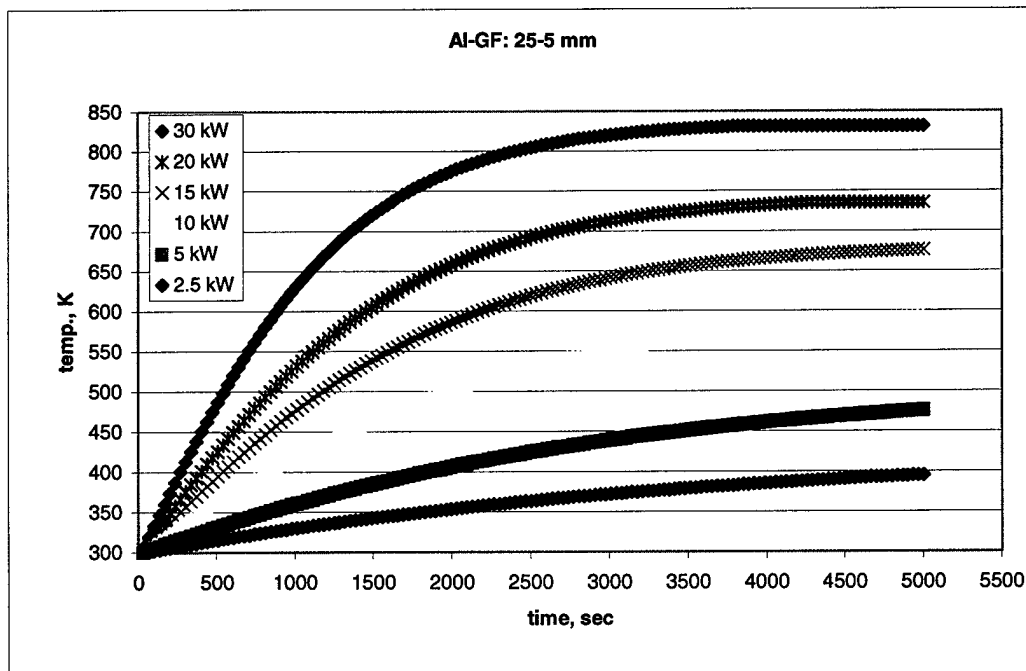


Figure 2.5 Transient heating curves for 12.5 mm thick Aluminum plate with 10mm thick glass fiber bed.

This analytical approach was also used to predict the temperature gradient throughout the thickness of the fiber preform, which was placed on top of the mold. This gradient needed to be controlled to within  $\pm 5^{\circ}\text{C}$  to ensure successful processing of the PBT material. This is crucial for infusing resin into the fiber preform due to viscosity variation and polymerization as a result of temperature difference. To predict the temperature gradient within the fiber preform with a reasonable degree of accuracy required a good estimate of the transverse thermal conductivity of the fiber preform. To establish the values for the thermal conductivity a small rig, shown schematically in Figure 2.6, was built.

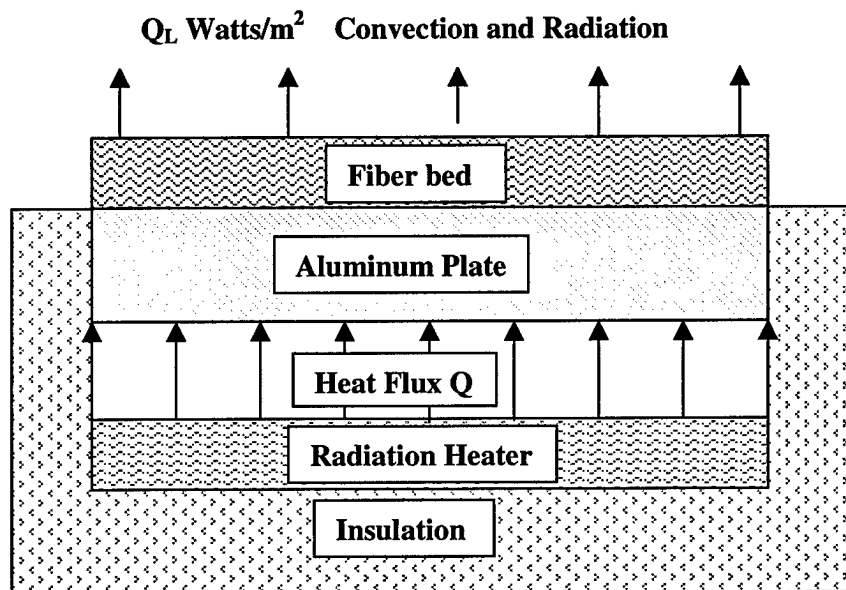


Figure 2.6 Schematic arrangement of the heat transfer apparatus

This rig used a 300x150mm aluminum plate, which was 25mm thick, together with a radiation heater covering the metal surface evenly. The heater, metal plate and the gap separating them were surrounded by solid insulation material made of calcium

silicates (marinite), which forced heat transfer in one direction, through the thickness. The thermal gradient of the fiber bed was characterized experimentally by inserting thermocouples between the different fabric layers. Figures 2.7 shows the temperature gradient across a glass fiber bed under vacuum while Figure 2.8 shows the same result for a carbon fiber bed under vacuum.

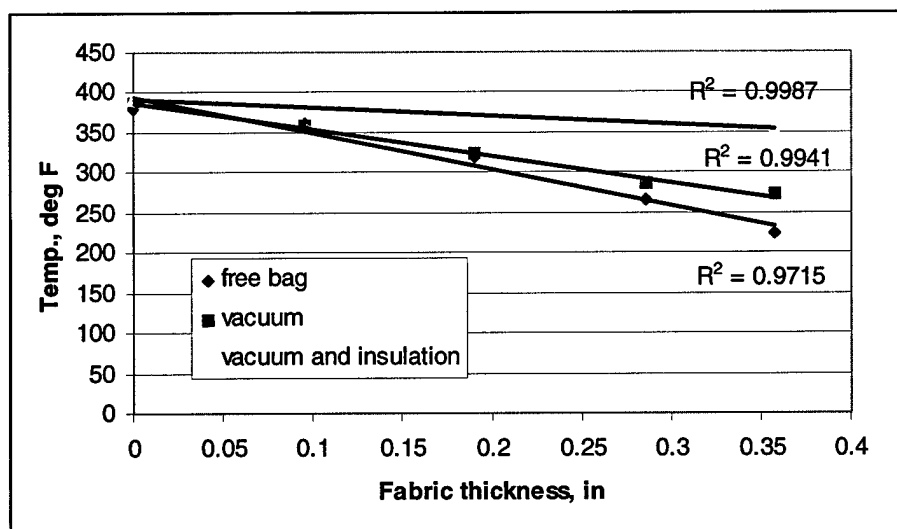


Figure 2.7: Measured temperature gradient through woven glass fiber bed

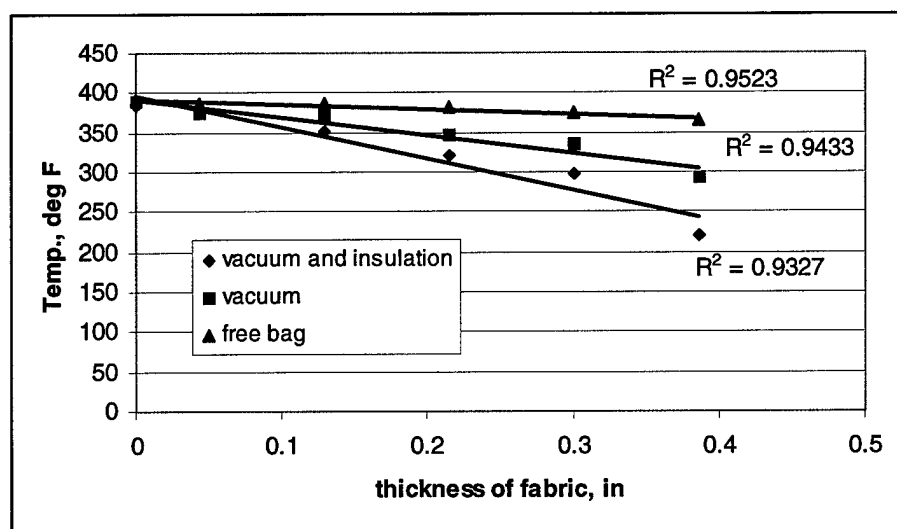


Figure 2.8: Measured temperature gradient through woven carbon fiber bed



To estimate the transverse thermal conductivity of the glass fiber bed under vacuum, the experimentally measured temperature gradient in Figure 2.7 was compared with the analytical curves in Figure 2.9.

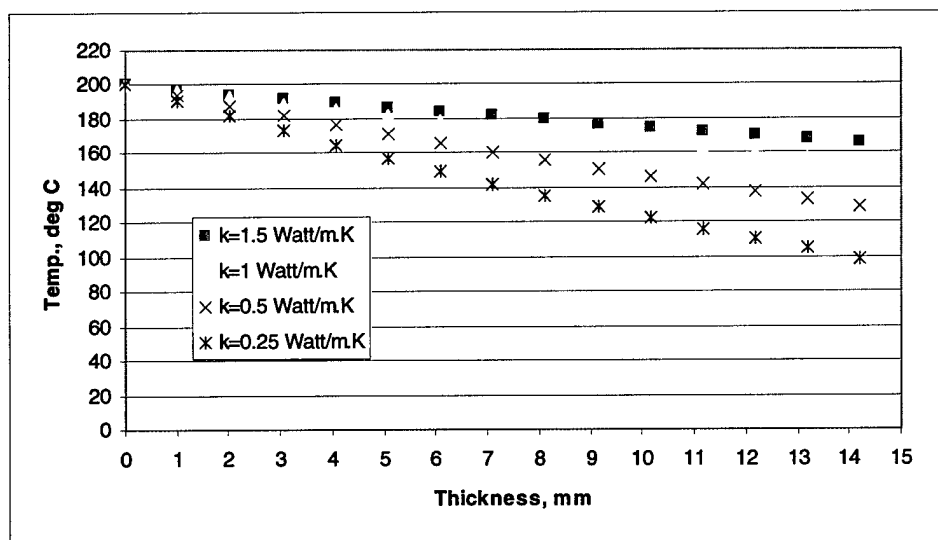


Figure 2.9 Calculated temperature gradient through glass fiber bed

The thermal conductivity used in the calculation of the temperature gradient, which matched the experimental gradient was chosen as the value for the thermal conductivity of the glass fiber bed. This value of  $0.75 \text{ Watts/m}^0\text{K}$  was taken to be a good approximation for the particular fiber bed under the experimental conditions. The same approach was used to estimate the transverse thermal conductivity for the carbon fiber bed. Figure 2.10 shows the predicted temperature gradients for a carbon fiber bed under vacuum which when compared with Figure 2.8, indicates that the thermal conductivity for carbon fiber was  $1.5 \text{ Watt/m}^0\text{K}$ .

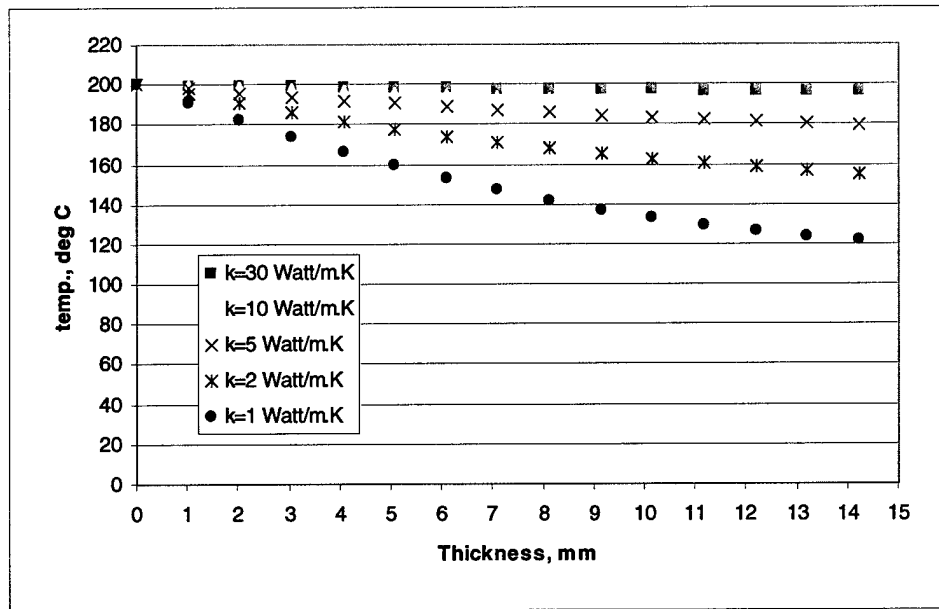


Figure 2.10 Calculated temperature gradient through carbon fiber bed

Table 2.1 shows the values for the thermal conductivity of both glass and carbon fiber beds under vacuum.

Fiber Bed		Thermal Conductivity Watt/m. <sup>0</sup> K
Glass	With Vacuum	0.75
Carbon	With Vacuum	1.5

Table 2.1 Thermal conductivity values for both glass and carbon fiber beds under vacuum

### 3.0 Elevated temperature VARTM process

#### 3.1 Equipment

The experimental set-up for elevated temperature VARTM of the thermoplastic prepolymer of PBT is shown schematically in Figure 3.1.

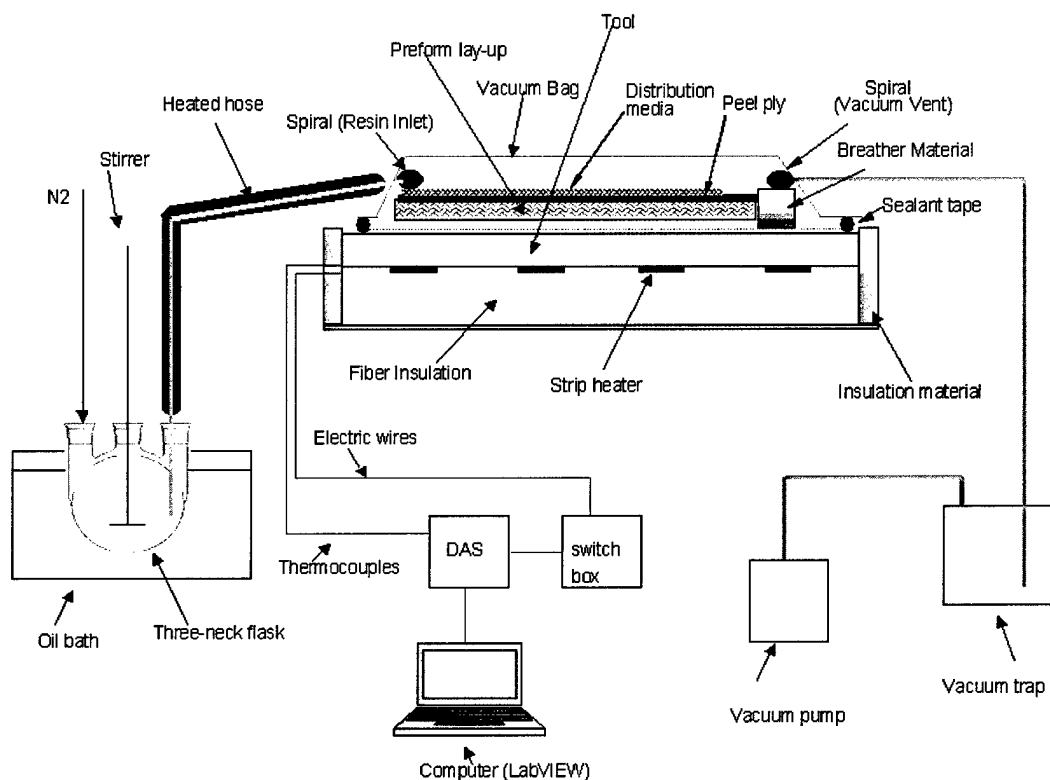


Figure 3.1 Layout of elevated temperature VARTM apparatus

It consisted of a flat heated mold, a system for melting and infusing the polymer into the fiber bed, a temperature controller and a data acquisition system. The mold was a 450mm square aluminum plate which was 12.5mm thick and was heated with 4x500Watt strip heaters. This heating capacity was equivalent to the 10kW/m<sup>2</sup> recommended in the thermal analysis section above. The temperature control was effected through a PID control system built on a LabVIEW platform operating on a

laptop computer. The temperatures were recorded using thermocouples feeding into the LabVIEW data acquisition system shown in Figure 3.2.

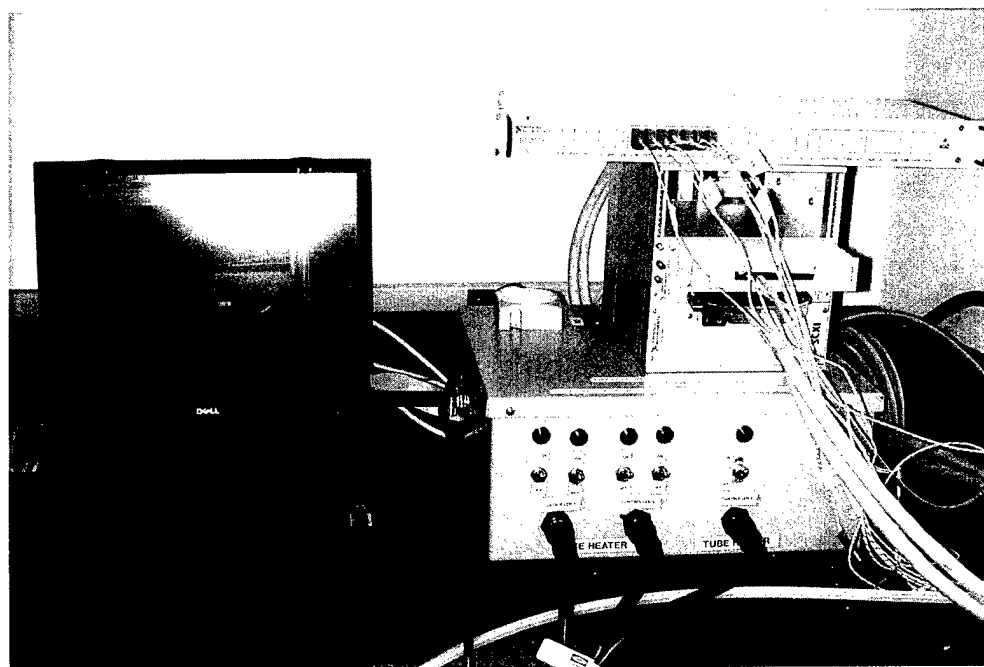


Figure 3.2 Temperature control and data acquisition system

The prepolymer was melted in a 1liter 3-necked glass flask immersed in a temperature controlled oil bath as shown in Figure 3.3. To mix the catalyst and prepolymer, the central neck accommodated a stirrer rod which was driven by a variable speed stirrer. The second neck was used to pass Nitrogen gas over the molten polymer to prevent oxidation while the third neck accommodated the delivery tube. When the prepolymer melt reached processing temperature the catalyst was added and the melt transferred under vacuum to the fiber perform via a heated transfer tube.

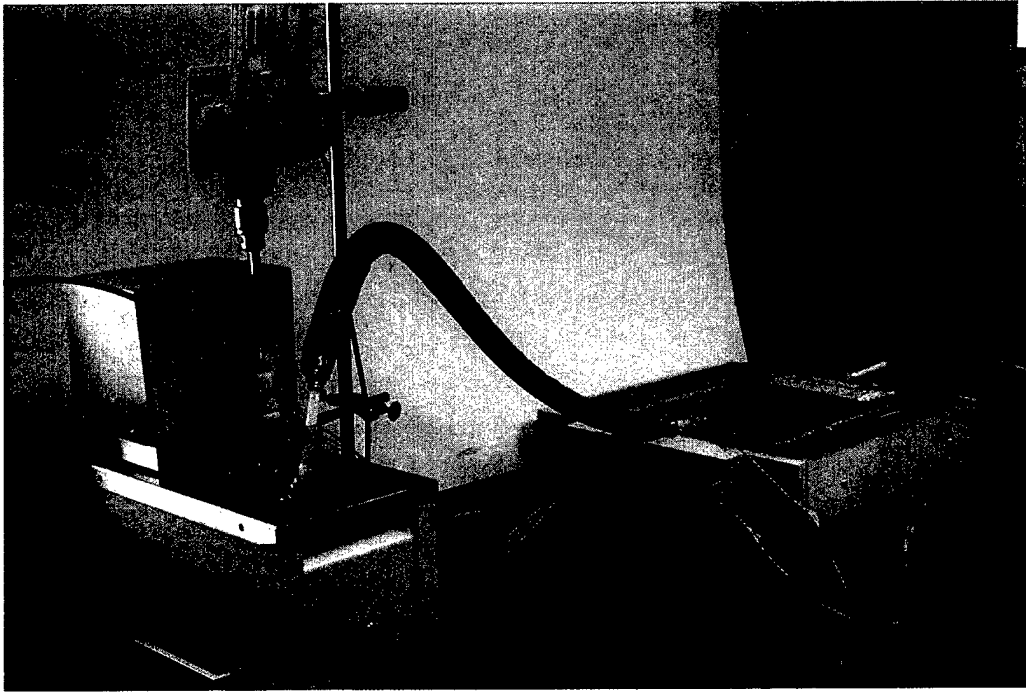


Figure 3.3 Polymer melting system and mold

The heated transfer tube shown in Figure 3.4 consisted of a disposable PTFE tube, which passed through a flexible metal tube, which had a silicon heater wound around it and insulated with suitable fiberglass sheathing.

All bagging materials, sealant tape, distribution media and disposable tubing were carefully selected to both withstand 200°C and not influence the polymerization of the PBT matrix that would take place within the mold.

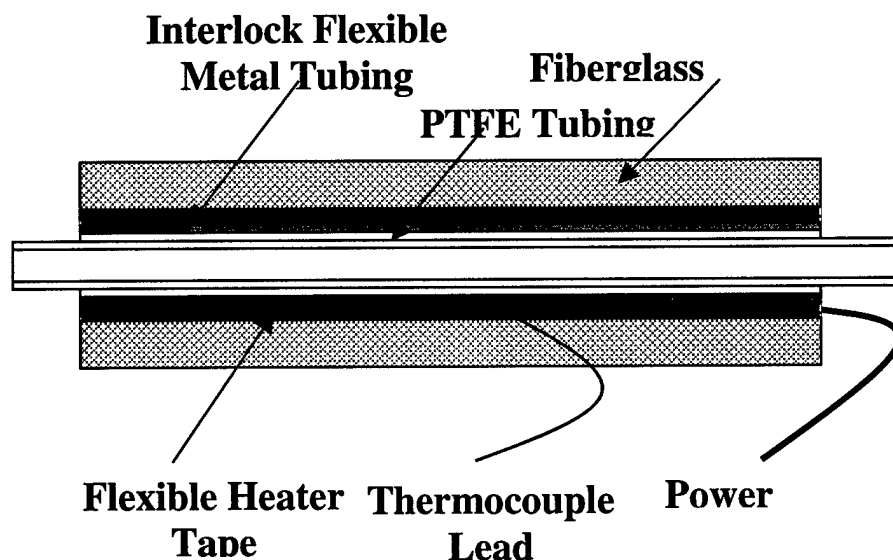


Figure 3.4 Flexible heated delivery tube

### 3.2 Processing of thermoplastic PBT

The heated mold surface was treated with a high temperature release agent (Airtech Safelease #30) and the fiber preform bagged with Airtech WN1500 Nylon film which had a temperature rating of 232<sup>0</sup>C. A Porous Teflon Coated Fiberglass Fabric bleeder cloth was placed on top of the fiber preform and on top of this was placed a stainless steel wire mesh, which acted as a fast track distribution media as shown in Figure 3.5. Vacuum was applied to the lay-up and the mold heated for a period to allow the preform to dry thoroughly prior to infusion of the molten resin.

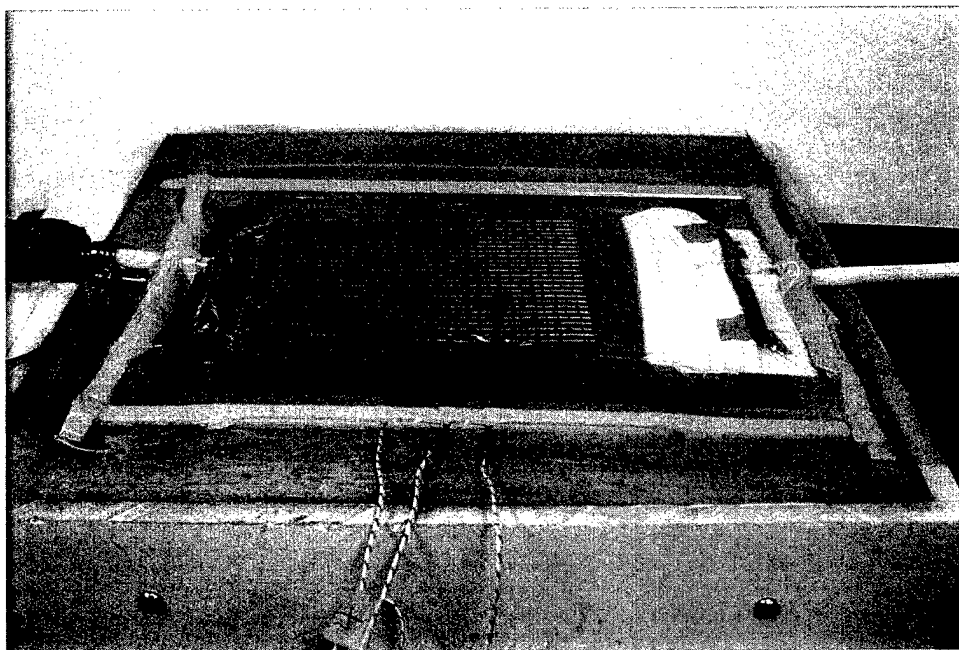


Figure 3.5 Lay-up prior to molding

The appropriate weight of the thermoplastic prepolymer, in the form of a powder, was placed in the flask and brought up to  $165^{\circ}\text{C}$  prior to the catalyst being added. A slight over-pressure of Nitrogen was maintained in the flask throughout the process.

After the catalyst was added mixing continued for about 2 minutes before the infusion process began.

A typical process cycle for the temperatures is shown in Figure 3.6.

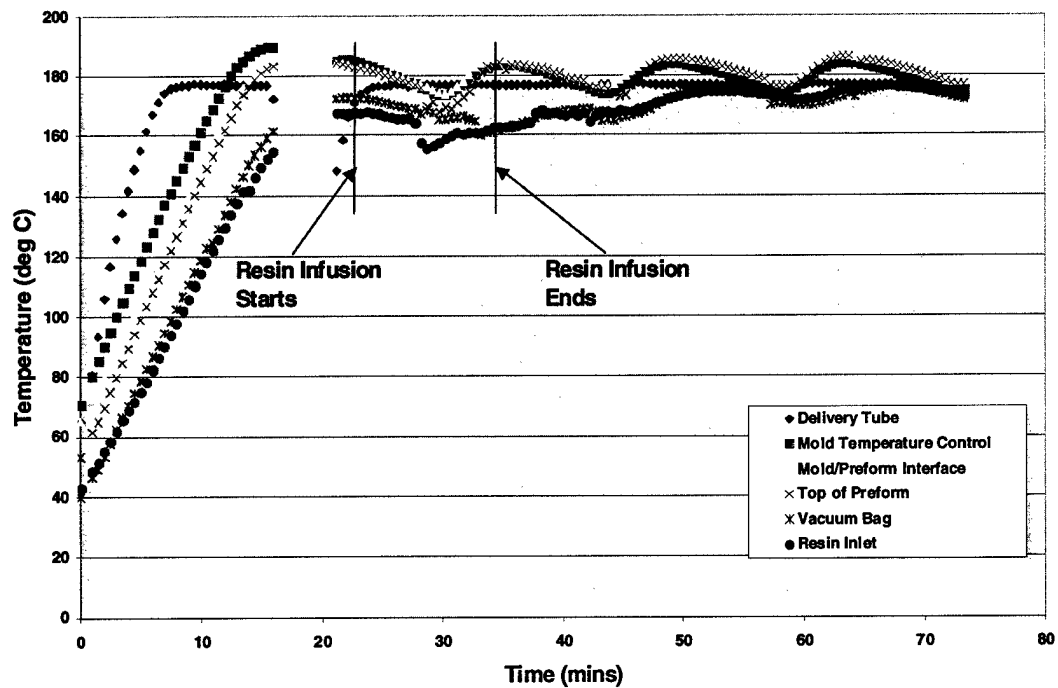


Figure 3.6 Temperature process cycle

The rate of infusion was dictated mainly by the permeability of the distribution media. When the infusion rate was too fast, the resin reached the vacuum port before sufficient resin was absorbed by the preform and evidence of this can be seen on the surface of the part shown in Figure 3.7. A slower infusion rate resulted in a completely filled part as shown in Figure 3.8

When the infusion process was completed, the part was held at 170°C for 40 minutes to allow the polymerization to reach completion. After this the part was demolded and prepared for evaluation.





Figure 3.7 Panel surface showing insufficient resin



Figure 3.8 Panel surface showing complete filling of the perform with resin

#### 4.0 Part Evaluation

The initial test that was carried out after molding was to take micrographs on selected sections, as shown in Figure 4.1, to establish if voids were present and complete fiber wetting took place. If the void content appeared to be low then molding of further parts continued as the process conditions were assumed to be satisfactory. The subsequent part evaluation program on a 3mm thick composite panel of woven S2 glass fiber reinforced PBT, included the following tests; fiber volume fraction, void content, DMA, DSC, GPC and flexure tests. This set of experiments, constitute a preliminary evaluation of panels made in the newly developed elevated temperature VARTM manufacture of thermoplastic composites.

The fiber volume fraction ( $V_f$ ) was measured using the burnout test and the results are shown in Table 4.2. A value of approximately  $V_f = 45\%$  was regarded as satisfactory at this early stage of development of the process. With improved control of the infusion process it should be possible to improve on this value.

An average value for the void content of the panel was also determined. First, the average density of the composite was experimentally determined by measuring the mass of five samples in water and calculating the volume of each sample. This experimental value for density was  $1.756 \pm 0.019 \text{ g/cm}^3$ . The calculated density of the composite was  $1.821 \pm 0.009 \text{ g/cm}^3$  based on the information obtained from the burnout test. The void content was calculated using these numbers and the following equations.

$$\Delta V = \frac{\Delta V}{1\text{gram}} = \frac{V_{\text{actual}}}{\text{mass}_{\text{actual}}} - \frac{V_{\text{calculated}}}{\text{mass}_{\text{actual}}} = \frac{1}{\rho_{\text{actual}}} - \frac{1}{\rho_{\text{calculated}}} \quad (1)$$

$$\% \text{void} = \Delta V * 100 * \rho_{\text{actual}} \quad (2)$$

The average value of void fraction was 3.6% as shown in Table 4.1. This was considered to be too high when compared to typical values of ---%, which are generally accepted for the room temperature VARTM process. Further process development will be required to reduce these values.

Sample Number	Fiber Volume Fraction, $V_f$ %	Void Fraction %
1	43.8	3.62
2	44.8	3.56
3	45.4	4.16
4	45.9	2.39
5	44.8	4.30
	Average $V_f = 44.95$	Average = 3.606
	Std. Dev. = 0.80	Std. Dev. = 0.752
	% Std. Dev. = 1.79	% Std. Dev. = 20.86

Table 4.1 Fiber Volume Fraction and Void Fraction of Glass Fiber/PBT panels

A TA-Instruments Dynamic Mechanical Analyzer 2920 with a three-point bend test fixture was used to obtain information about thermal properties and flexural modulus of neat PBT and its glass composite. Typical sample size was about 12-13 mm wide, 3-4 mm thick and 50 mm long. The heating ramp was fixed at 5 °C/min. Figure 4.2 shows the plot of flexural storage and loss modulus.

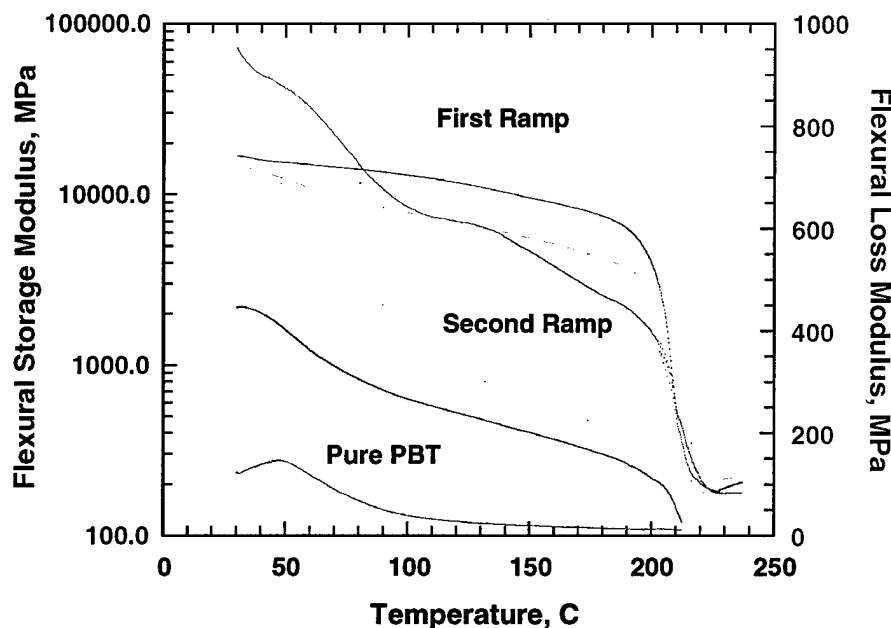


Figure 4.2 DMA measurements for Glass Fiber/PBT composite panel

The solid lines at the lower part of the plot, represents the results from neat PBT and the solid and dashed lines in the upper part represent the first and second heating ramp on the composite, respectively. The neat PBT could not be tested twice because the DMA bar melted and lost its shape. The modulus of both neat PBT and composite sample drastically drops at 210°C where PBT melts.

The storage modulus also decreases steadily above 60°C, which is the glass transition temperature ( $T_g$ ) of the PBT. The DSC thermogram of neat PBT also shows that there is a  $T_g$  in the region between 50°C and 60°C. Comparison of the first and second heat ramp of the composite sample shows that the storage modulus in the second ramp decreases faster than the first ramp does. Moreover, the loss modulus of the second ramp shows a single transition between 30°C and 100°C while the first loss modulus

shows a transition between 30°C and 100°C and another between 100°C and 150°C. These results agree with those obtained from DSC experiments. The DSC results showed that the crystalline structure of the PBT changed during annealing of the polymer above 220°C. The DMA results show that the annealing process also affects the flexural storage modulus. Further study is needed to determine the source of this transition and its correlation with the mechanical properties of the composite.

These DMA results show a storage modulus of approximately 18GPa at room temperature, falling to approximately 9GPa at 150°C on the first heating ramp. The loss modulus shows a glass transition temperature around 60°C.

Flexural tests were also carried out according to ASTM D790M and a flexural modulus of 18GPa (having a Std. Dev. of 4.5%) was obtained which agrees with the DMA results.

DSC measurements were carried out on the composite panels to investigate the melting point and the crystallization pattern. The results are shown in Figure 4.3 and it can be seen that there is a melting peak at 216°C on the first heating ramp and on cooling there is a crystallization peak at approximately 175°C. This would indicate that the mold temperature of 170°C used to mold these panels was a little too low to ensure a high degree of crystallization was achieved.

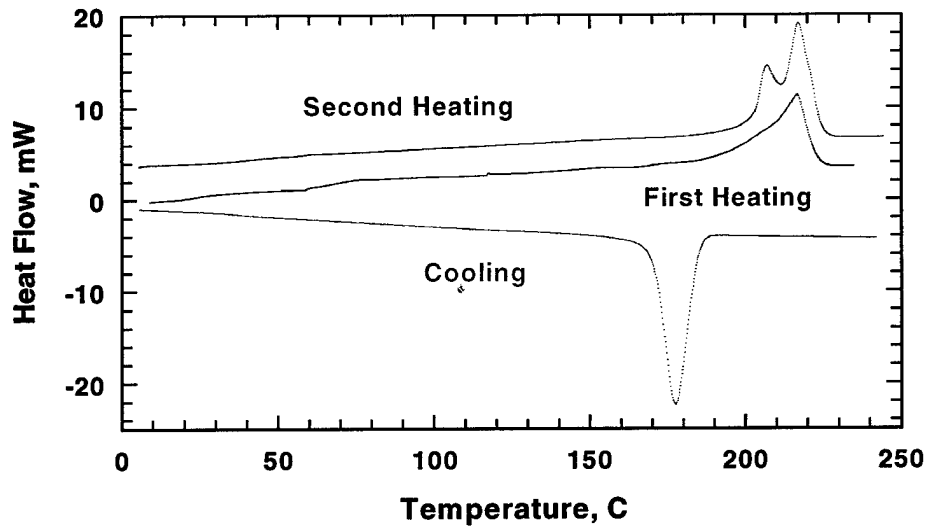


Figure 4.3 DSC measurements for Glass Fiber/PBT composite panel

GPC tests were carried out to determine the level of polymerisation that was achieved in the manufacture of the composite panels. The results show that polymerisation had only reached 65% of completion, which was probably due to the mold temperature being too low or the cure time being too short.

## 5.0 Conclusions

An apparatus was successfully developed for elevated temperature VARTM molding of thermoplastic composites.

The process window for molding a catalysed PBT prepolymer involved melting the prepolymer between 150 and 165°C. The time - temperature window for infusing the resin, in terms of viscosity, varied from about 10 minutes at 170°C to 60 minutes at 160°C.

The mold temperature for molding the PBT polymer should be above 170°C.

Comparison of DSC results between the PBT polymer and the PBT polymer within the composite indicated that the composition of the crystals was different in each case.

DMA results indicated that the flexural storage modulus at room temperature for the glass fiber/PBT composite was 18GPa. And this fell to 9 GPa at 150°C. Flexure tests confirmed the room temperature stiffness of 18GPa.

## Acknowledgements

The authors gratefully acknowledge the financial support from the Office of Naval Research. Thanks are also due to the Cyclics Corporation for the supply of materials and their technical help.

**Section II – Development of an Elevated Temperature VARTM  
system for a cyclic PBT and carbon fiber thermoplastic composite.**

**This work was carried out at the University of Delaware, during the period of  
March '02 to April '02.**



## **Development of an Elevated Temperature VARTM system for a cyclic PBT and carbon fiber thermoplastic composite.**

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Composites Research Unit, National University of Ireland, Galway, Ireland

### **1.0 Summary**

The following report details the work carried out at the University of Delaware, and the National University of Ireland, Galway, from 18<sup>th</sup> March to the 5<sup>th</sup> of April, 2002.

The purpose of this work was to build upon the work previously carried out at Delaware, (reported in Section I), using cyclic PBT and glass fiber. Primarily, the main goal was to investigate the processing of cyclic PBT with carbon fiber, and the mechanical properties of the final PBT/carbon fiber composite, and to compare that data to the data obtained previously, pertaining to cyclic PBT/glass fiber systems.

The National University of Ireland, Galway during this period, performed the following tasks:

- **Materials Selection and Acquisition**

The resin and catalyst system was supplied by the Cyclics Corporation and a detailed description of the materials is given. The carbon fiber was selected on the basis of compatibility data.

- **Cyclics PBT/Carbon fiber process investigation**

A detailed account of the vacuum assisted resin transfer molding procedure developed is given. This details the precise preparation of fiber and resin, required to perform the VARTM process.

➤ Manufacture of selected components

Samples of the selected configuration were molded using the molding procedure developed. The procedure is described in detail, and includes various observations and results.

➤ Mechanical Data

The samples processed at the University of Delaware were subjected to flexure testing and the results compiled and examined.

## 2.0 Materials Selection and Acquisition

Cyclics Corporation supplied the resin and catalyst system, which is described as XB0 95/5, that is 95% PBT, and 5 % PET. The 5% PET is added for economic purposes, and has negligible effects on the mechanical properties of the final composite.

The main factor affecting the selection of the carbon fiber for use with the cyclic PBT resin is that of sizing.

The sizing of every fiber is different and reacts differently with CBT – the sizing basically controls how the fibers react with matrices and are different due to the treatment they receive in order to help them react with different matrices. However the sizings are usually geared to Thermosets, and even sizings geared to thermoplastics can cause problems – most that claim to be suitable for thermoplastics, are geared to urethanes, and are not chemically suitable. Therefore all fibers must be subjected to a compatibility test before used in conjunction with CBT. Based upon this, Mitsubishi Carbon Fiber was selected due to its successful compatibility with cyclic PBT.

### 3.0 Process Review

The procedure developed for the manufacture of elevated temperature vacuum assisted resin transfer molding during this period is detailed below. The procedure is based upon observations and conclusions obtained through extensive research with cyclic PBT, both at the University of Delaware, and at the Cyclics Corporation.

The layout of the elevated temperature apparatus is described in figure 3.1, and the temperature control and polymer melting system can be seen in figures 3.2 and 3.3 respectively. The set-up of the apparatus almost identical to that used in Part 1 of this project, however, some observations and small changes were made.

The lay-up prior to molding is illustrated in figure 3.5. This lay-up uses a steel mesh as an interfacing medium between the resin and fiber perform. This interface has been known to cause some problems, in that the sharp edges can sometimes cause small ruptures in the nylon bagging, which compromises the vacuum. This in turn has serious detrimental effects on the mechanical properties of the final composite part.

The introduction of a nylon mesh led to the elimination of these issues. The nylon mesh also serves as an interfacing medium between the resin and the fiber, however it does not pose a threat to the nylon bagging, and therefore is a more reliable interface.

The nominal infusion temperature of cyclic PBT resin was found to be approximately 170°C, however, it was found that by heating the resin to 200°C and then cooling back down to 170°C, a 'hysteresis' effect on the viscosity of the resin was observed. That is, that as the resin cooled, its viscosity returned to a value lower than observed originally at 170°C, therefore leading to enhanced infusion of the fiber perform.

By heating the resin to 200°C, and then cooling, it also ensures that any moisture present in the resin, which may adversely affect polymerization, is removed before infusion of the fiber perform.

### 3.1 Procedure

The following procedure was devised in order to ensure repeatability of the process, and is based on supplier recommendations. The process has been amended as necessary, as the trials progressed.

#### **Procedure for VARTM processing of CBT at elevated temperature.**

**NOTE:** The material used for these trials is XB0 95/5, that is 95% PBT, and 5 % PET. The melting temperature of this material is 185C, but it is recommended that it be heated to 200C to ensure the material is fully molten.

- CBT is placed in a heating kettle (flask in a silicon bath) and heated to 200°C. Once the CBT reaches a temperature of 200°C, it should be fully molten and 'clear' in appearance. This temperature is maintained for 5-10 minutes to ensure that all moisture and solvent are removed. It is imperative that a vacuum or nitrogen purge is applied in order to prevent the CBT from oxidizing.
- The VARTM mold is cleaned, using plastic scrapers, and acetone.
- The mold is prepared by applying mold release, and when applied and dried, the fiber plies are added. Thermocouples are positioned strategically between the fiber layers in order to record temperature across the fiber bed, and form a temperature profile of the set-up.
- Mold preparation is completed by adding the interface, Teflon film, breather, tacky tape, and bagging. All sharp edges must be covered to prevent puncture

of the nylon bagging. (Use of nylon mesh will eliminate this risk.) Vacuum is applied to the lay-up, and the inlet tube to the molten CBT is clamped. The vacuum is examined to ensure that it is free of leaks, and is adequate.

- The fiber must be dried under vacuum at 170°C (based on the bed top temperature) for 1 hour. The bed top temperature of 170°C may be achieved by increasing the plate temperature, but it is important that the temperature of 190°C is not exceeded when introducing the molten CBT to the fiber bed.
- The temperature of the CBT is reduced from 200°C to 170°C. Ensure that the temperature is read from the resin, not the oil bath. The catalyst is added, once the resin has reached the optimum temperature, and there are no visible bubbles present in the molten CBT. (Visible bubbles are a sign that moisture or solvent is present in the molten material) The catalyst is mixed for approximately 1 minute – this may vary from one catalyst batch to the next, as some are ‘chunkier’ pieces, and some have been ground to a fine powder. Bubbles will appear once the catalyst has been added, and these are removed using a slight vacuum. Mixing is most efficient by varying the mixing speed once the catalyst has been added.
- Once the catalyst has been adequately mixed, and the fiber bed has been dried under vacuum for one hour and is at a temperature of 190°C, the inlet may be opened, and the CBT allowed to infiltrate the fiber bed. It is imperative that the temperature gradient between the plate temperature and the temperature of the top of the bed is minimal, and certainly less than 10 degrees. This is achieved using insulation –the bed ‘top’ temperature should be no more than 190C.

- Once the CBT has effectively infiltrated the fiber, the temperature is increased to 190C, (again, based on the top temperature) and allowed to cure for one hour.
- After one hour curing time, the part may be demolded.

**Points to Note:**

- Ensure that the inlet pipe is long enough to reach the bottom of the melting kettle, whilst still clamped.
- Ensure that the thermocouples are placed in position between the layers before commencing the process.
- Ensure that the temperature difference is less than 10 degrees BEFORE infusion.
- Ensure that the inlet pipe is at temperature before infusion.
- Ensure that system preparation is complete before adding the catalyst - catalyst can be mixed only for 1 minute, and then it must be infused, otherwise an increase in the viscosity of the CBT will occur, and therefore infusion will not be possible.

## 4.0 Manufacture of selected components

The following appendix describes in detail, the manufacture of the selected components over the course of 6 trials. Each trial describes the manufacturing methods used, relevant changes made, and theoretical values obtained.

### **Trial I:**

Date: 21/03/02  
Experiment Number: DEL1

### Details:

Resin: XB0 – P1 (95% PBT, 5% PET): 250g  
Catalyst: Fascat 4101 (0.22% by weight): 0.55g  
Fiber: S2 Glass Fiber, (8x12)", 4 Plies: 122.3g  
Plate Temperature during Infusion: 170°C  
Inlet Pipe Temperature during Infusion: 170°C  
Thermocouples: None Used  
Time required to mix Resin & Catalyst: 60 seconds  
Infusion Time: N/A

### Results:

This trial served the purpose of providing an introduction to the processing of CBT resin, and familiarisation of the high temperature VARTM process.

The temperature in the inlet pipe heating-jacket was not sufficient during this trial and so infusion was not successful in this case.



**Trial II:**

Date: 22/03/02

Experiment Number: DEL2

**Details:**

Resin: XB0 – P1 (95% PBT, 5% PET): 250g

Catalyst: Fascat 4101 (0.22% by weight): 0.55g

Fiber: Mitsubishi Carbon Fiber; 4 plies; (10x8)": 111.67g

Plate Temperature during Infusion: 170°C

Inlet Pipe Temperature during Infusion: 170°C

Thermocouples: (a) between layers 2 & 3; (b) top layer

Temperature Gradient - Top & Bottom layers: 6 degrees

Time required to mix Resin & Catalyst: 50 seconds

Infusion Time: 15 minutes

Curing Time: 1 hour @ 190°C

**Results:**

Weight of Fiber after Polymerisation: 149.61g

Fiber Volume (by Volume): 69%

Fiber Volume (by Weight): 75%

Grams Resin/Grams Fiber: 0.33

Resin Weight Fraction: 0.25

Resin Weight: 37.07g

**Visual Void Analysis:**

A large number of voids are clearly visible. In addition, a large dry spot is present, where the carbon fiber was not infused by resin. The position of this dry spot is in the same position where the thermocouples were placed.

The wire mesh caused a small rupture in the bagging during infusion, and this loss of vacuum is accountable for the high fiber volume, low resin volume, and dry spot encountered during this trial.

**Trial III:**

Date: 25/03/02

Experiment Number: DEL3

**Details:**

Resin: XB0 – P1 (95% PBT, 5% PET): 250g

Catalyst: Fascat 4101 (0.22% by weight): 0.55g

Fiber: Mitsubishi Carbon Fiber; 5 plies; (12x8)": 188.74g

Plate Temperature during Infusion: 190°C

Inlet Pipe Temperature during Infusion: 175°C

Thermocouples: (a) between layers 2 & 3;

(b) top layer

Temperature Gradient - Top & Bottom layers: 5 degrees

Time required to mix Resin & Catalyst: 30 seconds

Infusion Time: 5 minutes

Curing Time: 1 hour @ 190°C

Note: On the advice of Cyclics, the plate temperature was increased to 190°C during infusion, in order to allow the resin to infuse the fiber more easily.

### Results:

Weight of Fiber after Polymerisation:	276.3g
Fiber Volume (by Volume):	61%
Fiber Volume (by Weight):	68%
Grams Resin/Grams Fiber:	0.47
Resin Weight Fraction:	0.32
Resin Weight:	88.69g

### Visual Void Analysis:

A large number of voids are clearly visible on the surface of the panel, again, the wire mesh caused a small rupture in the bagging during infusion. An amount of resin was lost through the vacuum outlet, as the vacuum was applied for longer than usual in an attempt to let the assembly reach 'gel' time before the vacuum was shut off.

### Mechanical Testing:

Flexure tests were performed on all polymerised samples processed. See results section.

**Trial IV:**

Date: 27/03/02

Experiment Number: DEL4

Details:

Resin: XB0 – P1 (95% PBT, 5% PET): 250g

Catalyst: Fascat 4101 (0.22% by weight): 0.55g

Fiber: Mitsubishi Carbon Fiber; 5 plies; (11x8)": 165.52g

Plate Temperature during Infusion: 190°C

Inlet Pipe Temperature during Infusion: 175°C

Thermocouples: (a) between layers 2 &amp; 3; (b) top layer

Temperature Gradient - Top &amp; Bottom layers: 5 degrees

Time required to mix Resin &amp; Catalyst: 35 seconds

Infusion Time: 5 minutes

Curing Time: 1 hour @ 190°C

Note: The wire mesh used up to this point, was replaced by a nylon mesh in order to prevent further ruptures of the vacuum bagging. The nylon mesh was cut to size, and the edges softened with a blowtorch. Also, the outlet pipe was clamped in position, as it was found that as the plate temperature increased, the consistency of the 'tacky tape' used to seal the vacuum bagging became softer, and the rigid nature of the high temperature outlet tube tended to 'drag' the 'tacky tape', causing a violation of the vacuum. Thus, by clamping the outlet in position, it was hoped to avoid a reoccurrence of the event.

Results:

Weight of Fiber after Polymerisation:	270.17
Fiber Volume (by Volume):	54%
Fiber Volume (by Weight):	61%
Grams Resin/Grams Fiber:	0.63
Resin Weight Fraction:	0.39
Resin Weight:	104.18g

Visual Void Analysis:

The visible void content was seemingly low – no obvious voids were noted. A point to note during this trial, is that the vacuum was again compromised during infusion, although the cause is not certain.

Mechanical Testing:

Flexure tests were performed on all polymerised samples processed. See results section.

**Vacuum Study:**

The violation of the vacuum during infusion has been the main problem to date, therefore, a study was undertaken before the next trial.

A 'double tape' method was used to bag an assembly, that is, General Sealants white sealant tape, maximum temperature of 177°C was used in conjunction with General Sealants green sealant tape, which operates from 177°C upwards. No mesh or thermocouples were used, and the assembly remained under vacuum for 30 minutes, at 170°C, at a vacuum pump pressure reading of 28mmHg.

This assembly was used again on April 1st, this time using mesh and thermocouples, and a loss of 10 mmHg in 15 minutes occurred. It was thought that perhaps the thermocouples might be allowing air to escape.

It was found that both GS tapes were very soft in consistency when heated, and tended to be dragged inward once the vacuum was applied, sometimes shifting inlet or outlet pipes in the process, or sometimes the thermocouples.

SM Black Tacky tape, with a maximum temperature of 204°C seemed more robust, and a study was conducted with this. A vacuum pressure of 28mm Hg was maintained at 170°C for 40 minutes with the nylon mesh included in the assembly, and indeed was also maintained overnight at room temperature, without any loss of vacuum.

Therefore it was decided to use this tape in future trials.

**Trial V:**

Date: 02/04/02

Experiment Number: DEL5

**Details:**

Resin: XB0 – P1 (95% PBT, 5% PET): 250g

Catalyst: Fascat 4101 (0.22% by weight): 0.55g

Fiber: Mitsubishi Carbon Fiber; 5 plies; (10x8)": 155.56g

Plate Temperature during Infusion: 172°C

Inlet Pipe Temperature during Infusion: 170°C

Thermocouples: None

Temperature Gradient - Top & Bottom layers: 1 degree

Time required to mix Resin & Catalyst: 30 seconds

Infusion Time: 7 minutes

Curing Time: 1 hour @ 190°C

Note: The thermocouples were omitted, as it was thought that they may have contributed to the loss of vacuum. The SM Black tacky was used to replace the GS tape that had been used prior to this trial. The plate temperature was decreased back to 170°C as it was suggested that the gradient from the resin bath (170°C), through the heated inlet pipe (170°C) to a plate temperature of 190°C, may have affected the infusion patterns adversely.

Results:

Weight of Fiber after Polymerisation:	219.22
Fiber Volume (by Volume):	64%
Fiber Volume (by Weight):	71%
Grams Resin/Grams Fiber:	0.42
Resin Weight Fraction:	0.29
Resin Weight:	64.65g

Note: The nylon mesh absorbed quite an amount of resin – the combined weight of the resin infused on the mesh was 85 g, therefore, by not accounting for the resin taken up by the nylon mesh, insufficient resin remained to fully infuse the carbon fiber, concluding in a high fiber volume panel. The vacuum was maintained throughout this trial.

Visual Void Analysis:

The visible void content was seemingly low – the vacuum was not compromised throughout the trial. However, as mentioned, the nylon mesh absorbed a good deal of resin, which lead to a high fiber volume part.

Mechanical Testing:

Flexure tests were performed on all polymerised samples processed. See results section.



**Trial VI:**

Date: 03/04/02  
Experiment Number: DEL6

**Details:**

Resin: XB0 – P1 (95% PBT, 5% PET): 275g  
Catalyst: Fascat 4101 (0.22% by weight): 0.605g  
Fiber: Mitsubishi Carbon Fiber; 5 plies; (8x8)": 125.85g  
Plate Temperature during Infusion: 190°C  
Inlet Pipe Temperature during Infusion: 170°C  
Thermocouples: None  
Temperature Gradient - Top & Bottom layers: 3 degrees  
Time required to mix Resin & Catalyst: 30 seconds  
Infusion Time: 6 minutes  
Curing Time: 1 hour @ 190°C

Note: From the previous trial, it was found that the nylon mesh absorbs a certain amount of resin, therefore, in order to account for this, two factors were changed in this trial. The first is that the length of the mesh was reduced to half the length of the fiber bed. It was proposed that for a small part, it is not necessary to maintain the interface mesh length equal to that of the fiber bed, but other factors lead to this conclusion. Decreasing the length of the mesh decrease the amount of resin that is required, as less resin will be absorbed, and previously, the it had been noted that the resin flowed across the top of the mesh and did not infuse the fibers very efficiently, therefore, the decreased path of interface mesh should encourage the resin to infiltrate

the fibers. The second is that the amount of resin per area of fiber was increased according to the predicted amount of resin likely to be absorbed by the nylon interface mesh. A last item to note, is that the plate temperature was increased to 190°C during infusion, as this should increase decrease the viscosity of the resin and aid infusion.

#### Results:

Weight of Fiber after Polymerisation:	193.95g
Fiber Volume (by Volume):	58%
Fiber Volume (by Weight):	65%
Grams Resin/Grams Fiber:	0.54
Resin Weight Fraction:	0.35
Resin Weight:	63.34g

#### Visual Void Analysis:

The visible void content was seemingly low – the vacuum was not compromised throughout the trial.

#### Mechanical Testing:

Flexure tests were performed on all polymerised samples processed See results section.

## 5.0 Mechanical Testing - Results

### 5.1 Introduction:

All carbon fiber panels were subjected to flexure testing in NUIG based on the ASTM standard - ASTM D 790-92. This test is used to determine the outer fiber strength and Young's modulus of the composite material.

Four samples were taken from each carbon fiber panel - the recommended number is 5, however due to the limited size and number of panels, it was decided that four samples was sufficient. The preparation of the samples is as follows:

#### Test Specimen:

Depth: 3.5 mm

Therefore from ASTM D 790-92, TABLE 1; the recommended dimensions based on the given thickness, and a 32/1 L/d ratio are:

Width: 25 mm

Length: 130 mm

Support Span: 100 mm

Rate of Cross Head Motion: 5.3 mm/min

Number of Specimen: 5

## 5.2 Summary of Results:

Table 5.1: Summary of Flexural Data

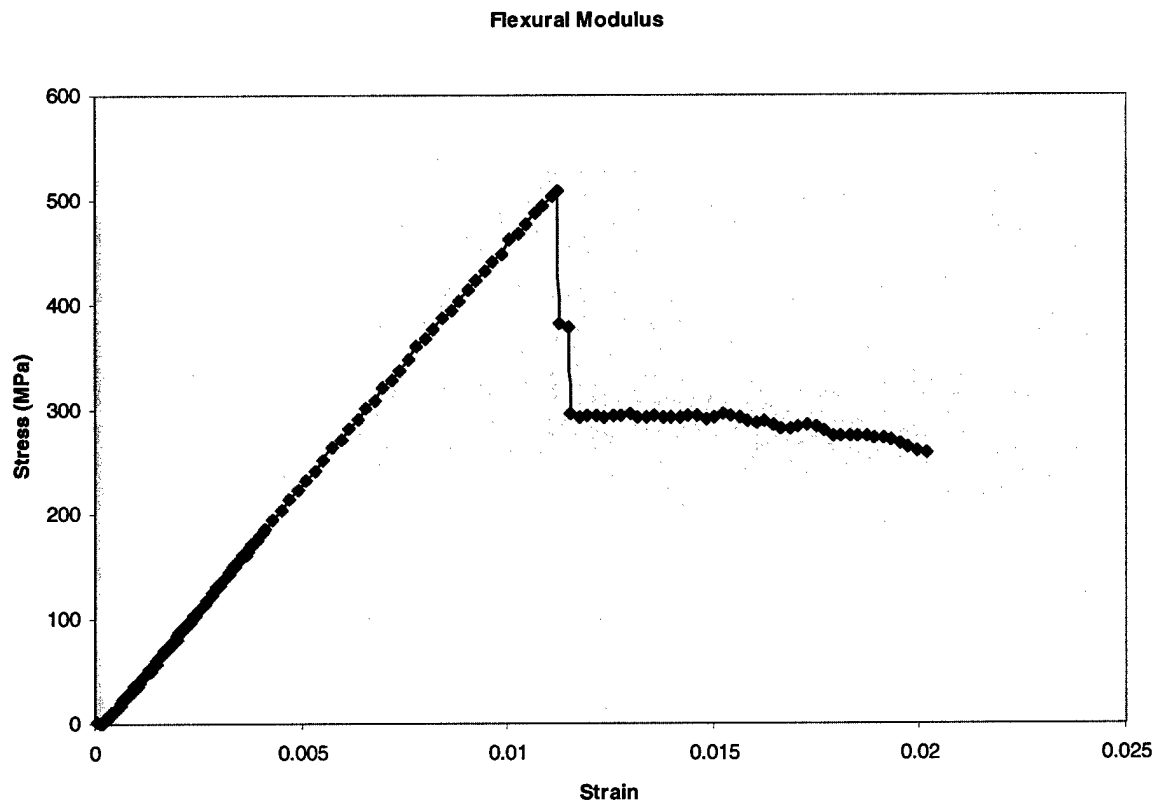
Sample Code	Thickness (mm)	Width (mm)	Yield Strain (mm/mm)	Stress (MPa)	Yield Displacement (mm)	Max Load (kN)	Modulus (MPa)
DEL3-01	3.1	25.1	0.0112	508.9	6.022	0.8183	47280
DEL3-02	3.1	25.1	0.0085	381.1	4.554	0.6129	51410
DEL3-03	3.1	25	0.0088	432.7	4.745	0.6931	50820
DEL3-04	3	25	0.0099	480.9	5.518	0.7213	53590
DEL4-01	3.4	25.1	0.011	385.5	5.398	0.7458	44710
DEL4-02	3.4	25.2	0.015	358	7.358	0.6952	46020
DEL4-03	3.4	25.1	0.0133	404.8	6.495	0.783	40850
DEL4-04	3.4	25.2	0.0112	420.1	5.466	0.8158	42890
DEL5-01	3	25.1	0.0081	307.1	4.508	0.4625	45670
DEL5-02	3	25	0.0107	407.7	5.941	0.6115	47350
DEL5-03	3	25.1	0.0109	482.2	6.045	0.7262	45740
DEL5-04	3	25.1	0.0103	392.2	5.718	0.6966	46820
DEL6-01	3.2	25	0.0128	453.3	6.652	0.7737	45410
DEL6-02	3.2	25	0.0123	440.6	6.385	0.752	45730
DEL6-03	3.2	25	0.0101	432.8	5.237	0.7387	45580
DEL6-04	3	25	0.014	353.6	7.797	0.5304	32880

Sample	Theoretical VF (%)	Av. Flexure Strength (Mpa)	SD	Av. Max Load (kN)	SD	Av. Modulus (GPa)	SD
DEL3	61	450.9	56.2	0.7114	0.085	50.775	2.617
DEL4	54	392.1	26.8	0.75995	0.052	43.617	4.866
DEL5	64	397.3	71.8	0.6242	0.118	46.395	1.723
DEL6	62	420.1	45.1	0.6987	0.113	42.4	5.842

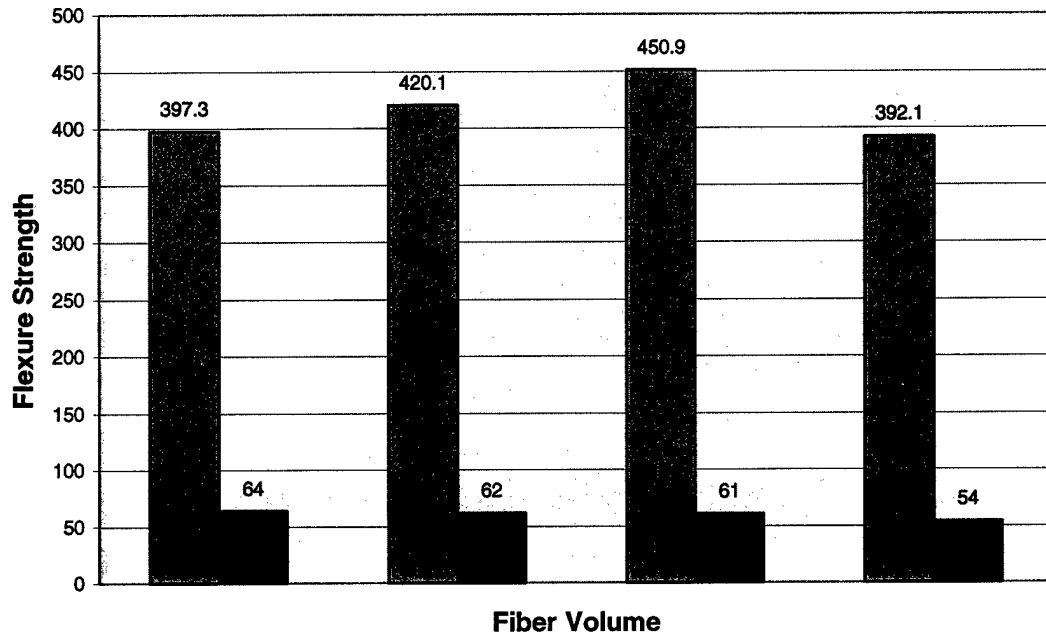
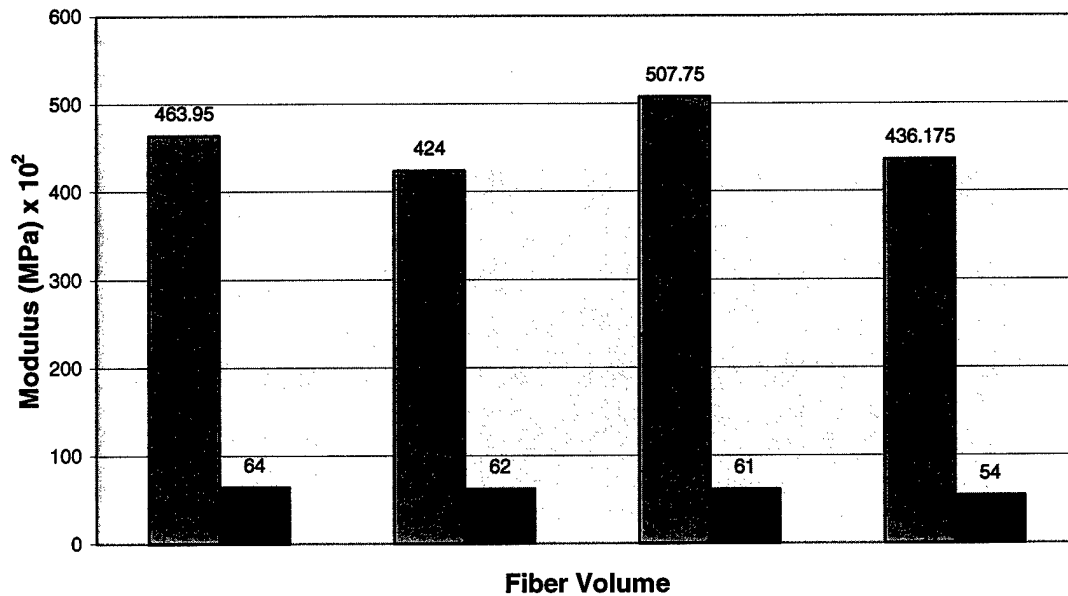
Table 5.2: Standard Deviation of Flexural Data in all samples, where SD = Standard Deviation, and Av. = Mean

### 5.3 Graphical Results:

The following figure illustrates a typical plot of Stress versus Strain, and clearly shows the maximum flexural stress point. Each sample tested generated a plot similar to this.



The following figures demonstrate the effect of fiber volume on Flexural Modulus and Flexural Strength respectively, for the five carbon fiber reinforced CBT panels manufactured.

**Flexure Strength v's Fiber Volume****Modulus v's Fiber Volume**

## 6.0 Conclusions

A working process window was developed for the elevated temperature vacuum assisted resin transfer molding of cyclic PBT and carbon fiber. Several composite parts were successfully manufactured and tested.

The nominal infusion temperature of cyclic PBT resin was found to be approximately 170°C, however, it was found that by heating the resin to 200°C and then cooling back down to 170°C, a 'hysteresis' effect on the viscosity of the resin was observed. That is, that as the resin cooled, its viscosity returned to a value lower than observed originally at 170°C, therefore leading to enhanced infusion of the fiber perform.

Examination of flexure testing results show, that a PBT/carbon fabric composite has a flexural modulus as high as 50.8 GPa at room temperature, and a flexure strength of as high as 450 MPa.



### **Section III - Development of a Polyamide Copolymer Resin Transfer Molding System for Thermoplastic Composites**

**This work was carried out at the National University of Ireland Galway, during  
the period of September '01 to September '02.**

## **Development of a Polyamide Copolymer Resin Transfer Molding System for Thermoplastic Composites**

**Mark Greaney, Conchúr Ó Brádaigh**

Composites Research Unit, National University of Ireland, Galway, Ireland

### **Abstract**

The applicability of reinforced polyamide copolymers as a matrix for advanced composites was assessed. The copolymer consisted of an anionically polymerised PA 6/12 mixture. Resin Transfer Molding, or RTM, was used to impregnate a dry fiber bed. The low viscosity resin was forced into a mold cavity, flowed around the fibers, and polymerised to form solid composite structure. The system employs an activator and catalyst which, when combined with a co-monomer melt, formed a copolymer in-situ. The entire process was completed in a matter of minutes.

Direct impregnation of reinforced-reinforced composites by a liquid matrix allows large, complex, and repeatable parts to be fabricated with low tooling costs and cycle times. As opposed to thermosets, thermoplastic matrices offer the advantages of high impact strengths and the ability to be recycled. Due to high melt viscosities, thermoplastics are generally not used for high volume fraction resin injected parts. The employment of an activated melt, which polymerises in-situ, overcomes this problem. The process relies on two monomers, caprolactam and laurolactam, which when combined with an activator and catalyst form the copolymer polyamide 6/12.

A desktop heated composite tool was designed and used to create both reinforced and un-reinforced plates. Different mixtures of PA-6 and PA-12 were investigated to establish their physical and mechanical properties. Plates were also created on an industrial sized hydraulically controlled composite press. The effect of processing pressure was monitored using this tool.

Mechanical and physical tests were carried out at the University of Ireland, Galway. Mechanical tests included tensile, flexure, and impact testing. Physical tests consisted of Digital Scanning Calorimetry and moisture absorption.

## 1. Introduction

Modern composites, or advanced composites, are composed of high performance fibers and a polymer matrix that binds the fibers together. The matrix serves two primary functions; firstly it protects the fibers from any hazardous conditions to which it may be exposed, and secondly it unites the fibers so that any loads may be distributed over a maximum possible area. Advanced composites are used in almost every field of engineering. Their applications include construction, aeronautical, aerospace and, automotive to name just a few.

Currently, thermoset-based resins dominate the advanced composite market. However thermosets have several intrinsic disadvantages that in today's environmentally aware society are become increasing problematic. The two most prevalent problems with thermosets are their inability to be recycled and the harmful emissions that can be produced during processing. Thermoplastics on the other hand, can be recycled and do not have any harmful by-products. In addition to this they can be remolded and welded. Furthermore thermoplastics have much better toughness and impact resistance than their thermoset counter parts.

The goal of the project is to create lightweight high performance parts for use primarily in the automotive industry. The material therefore must:

- Have a very high strength to weight ratio
- Be dimensionally stable
- Be able to be processed economically i.e. quickly and cheaply

- Be able to form complex shapes
- Be recyclable

The matrix chosen to fulfill these requirements was anionically polymerised lactam 6/12 (APLC 6/12), a thermoplastic co-polymer. Caprolactam and laurolactam, the precursors to polyamide 6 and polyamide 12 respectively, were chosen for their ease of processing and their history of success as engineering polymers. The reinforcement chosen for the composite was carbon fiber.

Note: Nomenclature: Polyamide has been abbreviated as PA. The number after PA refers to the particular polyamide material e.g. PA 12 = polylaurolactam and PA 6 = polycaprolactam. For copolymers the mixture of polylaurolactam and polycaprolactam is referred to as PA 6/12. To simplify the terminology a mixture of 90% polycaprolactam and 10% polylaurolactam would be shortened to 90/10 PA 6/12. In certain circumstances the trade name Nylon is used to refer to a polyamide polymer.

## 2. Nylon & Anionic Polymerisation

Polyamides are more commonly known as Nylons. In October 1938 DuPont introduced the first nylon polymer to the commercial market, poly(hexamethylene adipamide), or PA 66. Nylon's breakthrough came because of its ability to replace metals in certain applications due to its high mechanical and physical properties. These include its toughness and resistance to abrasion. It can also be formed into high strength fibers. For these reasons it was considered to be the first "engineering thermoplastic." [1]

<u>Advantages</u>	<u>Disadvantages</u>
<ul style="list-style-type: none"><li>• Excellent Mechanical Properties</li><li>• Good Temperature Resistance</li><li>• Good Chemical Resistance</li><li>• Low Friction</li><li>• Toughness</li><li>• Abrasion Resistance</li></ul>	<ul style="list-style-type: none"><li>• Expensive</li><li>• Some Grades Moisture Sensitive</li></ul>

Table 1. Brief Overview of Polyamide Materials

It is sometimes beneficial to mix two polyamide polymers to form a copolymer. The optimal copolymer would take the best properties, applicable to the particular situation, from each polymer to create a material that is ideally suited to its intended purpose. This project focused on PA 6/12 copolymers and investigated the various differences in both the physical and mechanical properties. The overall goal of the project was to find a suitable matrix for carbon fiber reinforced composites. While extensive research has been done on hydrolytically polymerised PA 6/12, this project is unique in that it analyses anionically polymerised 6/12 for use as a matrix in an advanced composite.

Anionic polymerisation is a quick and clean method of producing polyamide materials. Conversion to high molecular mass polymer is almost instantaneous. All that is required is the pre-polymer, catalyst, activator and a means to heat and mix them together. It has a well-documented history of success dating back to 1941. [1]

Thermoplastic composites utilising APLC 12, Anionically Polymerised Lactam Composites, were developed at EMS Chemie AG, Domat-Ems, Switzerland. It was at this facility that the activator and catalyst solution was created. It was called GRILONIT. The solution is sensitive to UV radiation and moisture, but otherwise requires no special storage conditions. Also, it does not decay significantly over long periods of time. After a period of six months of repeated usage the GRILONIT showed no visible degradation and still continued to produce plates with good polymerisation.

EMS Chemie, using a purpose built mixing and injection machine as an impregnation tool, created APLC 12 reinforced composites. The composites manufactured were of high quality and exhibited good wetting, minimal void content, and good

polymerisation. However APLC 12 does not have many of the benefits associated with some of its close Nylon relatives, particularly Nylon 6.

Nylon 6 has higher tensile and flexural strengths than Nylon 12. It also has a higher melting point and costs significantly less. So why not create a reinforced APLC 6 composite? While Nylon 6 does have the benefits listed above it does have several drawbacks, the most of important of these being its impact strength and its moisture absorption. Nylon 6 can absorb up to 9.5% moisture by weight, which for many purposes is not acceptable. Nylon 12 does not have these problems, its impact strength is considerably higher and it absorbs approximately only 1% of its weight in moisture. Because of these properties it was thought that a Polymer Matrix Composite (PMC) composed of a Carbon Fiber-APLC 6/12 matrix could outperform that of a Carbon Fiber-APLC 12 composite.

The idea was to create a suitable polymer with high mechanical properties and low moisture absorption. As will be disclosed later on it is not possible to have the "ideal" co-polymer. As in most engineering design, compromises must be made. For instance, adding 30% laurolactam to the caprolactam melt decreases moisture absorption significantly and only lowers its melting point by a few degrees. However it decreases the tensile, flexural, and compressive strengths greatly. Therefore we can predict that there is not an ideal co-polymer for all applications, however; you can tailor make a suitable co-polymer for a given set of loading conditions.



PA 6/12 (mol/mol)	T <sub>m</sub> (°C)	Tensile Strength (MPa)	Elongation at Break (MPa)	Young's Modulus (MPa)	Density (g/cm <sup>3</sup> )	T <sub>g</sub> (°C)
0/100	178.0	54	200-300	1180	1.008	42
10/90	168.7	50	304	1080	1.011	33
20/80	159.7	52	337	830	1.018	27
40/60	138.5	53	358	390	1.035	22
50/50	137.5	N/A	N/A	N/A	1.045	20
60/40	138.7	55	380	260	1.055	29
80/20	180.5	59	375	440	1.087	35
90/10	201.8	57	307	1370	1.108	36
100/0	222.8	61	250	2410	1.131	48

Table 2. Typical Properties of PA 6/12 Copolymers [1]

### 3. Reinforcing Material

Carbon Fiber Fabric (2/2 Twill) was used for all reinforced processing and testing. The fabric has a weight of  $440 \text{ g/m}^2$ . It is coated with a polyamide 6/6 sizing that does not affect the polymerisation process. The sizing is a very important part of the reinforcement when the Grinolit anionic polymerisation system is employed.

Many different types of fibers and fabrics were tested to determine compatibility at EMS Chemie. Unfortunately the sizing that is normally applied to glass fibers corrupts the process. There has however, been some success with glass-APLC 12 using a special preparation before using the APLC processing system. Basically it involves "burning off" the original sizing and replacing it with a compatible one. Currently there are no fiber producers that create glass with an appropriate sizing

## **4. Equipment**

In order to investigate the applicability of the PA 6/12 copolymer, 27 plates were fabricated. From these plates over 400 specimens were cut and tested. The material processing was carried out in the laboratories of NUI, Galway. Plates were created using two heated composites molds. Technicians in the Heavy Machine Laboratory cut specimens according to the specific ASTM standard. Testing was carried out in the Department of Engineering and the Department of Chemistry at NUIG as well as at the commercial company, Composites Testing Laboratory LTD. (CTL).

### **4.1 Processing Equipment**

The basic requirements for the VARTM co-polymer system are that:

- 1) The monomers can be melted under an inert atmosphere.
- 2) The monomers, activator, and catalyst can all be mixed thoroughly prior to injection.
- 3) The tool must be airtight during impregnation and polymerisation.
- 4) The tool must be able to hold a constant temperature for a period of time and then cool down [2]

To melt the monomers, a standard laboratory hot plate was used. A Silicon oil bath was placed on top of the plate. In order to evenly distribute the temperature throughout the oil, a magnetic stirrer was used. A 500 ml beaker placed directly into

the heated Silicon oil contained the monomers during the melt process. Nitrogen was fed into the beaker through a two holed rubber bung. Another magnetic stirrer placed in the beaker mixed the caprolactam and the laurolactam and helped to distribute the temperature throughout the melt evenly.

## 4.2 Composite Tool

The mold used in these trials is a modified heated composite tool. It consists of two aluminium plates, heating elements and a picture frame cavity. A control box containing a digital temperature readout, heater switch, and safety cut off, regulates the system. The entire unit is portable and weighs less than 30 Kg. It is capable of producing high quality repeatable reinforced and un-reinforced plaques. The usable plate area is 330 mm x 300 mm.

The plate temperature is monitored by a K type thermocouple. This thermocouple, imbedded in the centre of one of the plates, indicates the temperature on the control box display allowing precise monitoring and control of temperatures. The heating rate is 15 degrees C per minute.

The mold cavity is created by inserting a picture frame in between the two plates. The size of the cavity, and therefore the part thickness, can be modified by utilising picture frames with different thicknesses. The picture frame used for these trials was made of aluminium and is 2 mm thick.

In order for VARTM to be possible there must be an airtight seal. The plates have square channels milled just inside the perimeter. In these channels rubber tubing is inserted. The tubing is compressed against the entire picture frame perimeter on

either side creating the seal. To fasten the mold together 21 bolts are used which applies a limited amount of pressure on the fiber bed.

The heating system was developed by PPA Teo. in Carraroe, Ireland. It consists of ribbon resistance heaters bonded in a thermoset. This mixture is held against the aluminium plates by a spring system bolted to a rigid back. As the heating elements increase in temperature they expand the thermoset inducing strains. This expansion pulls the material away from the plates. The spring system holds the heating elements against the plates.

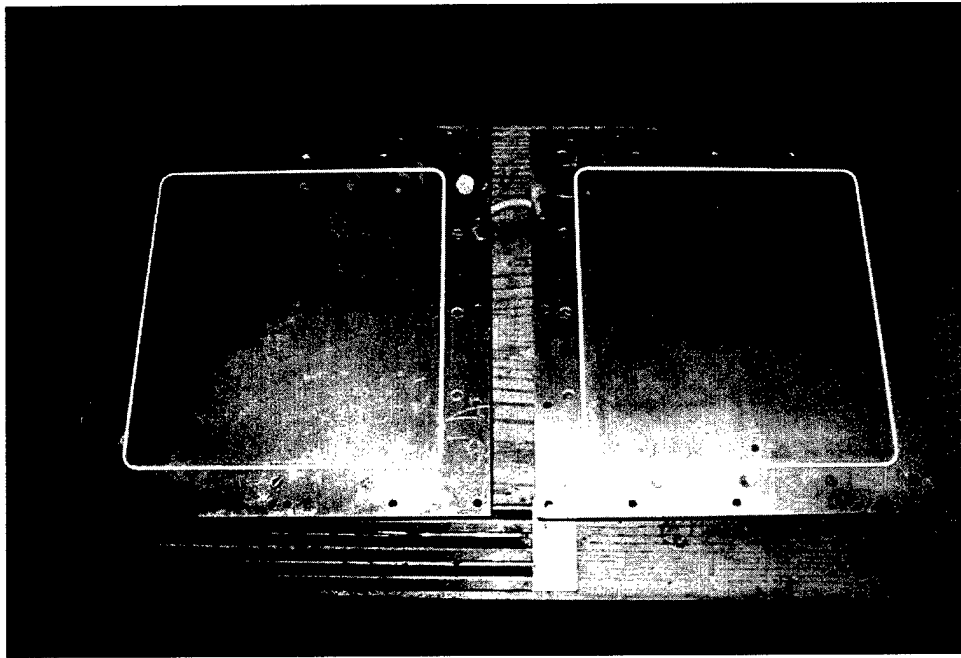


Figure 1. Heated Composite Tool (Open)

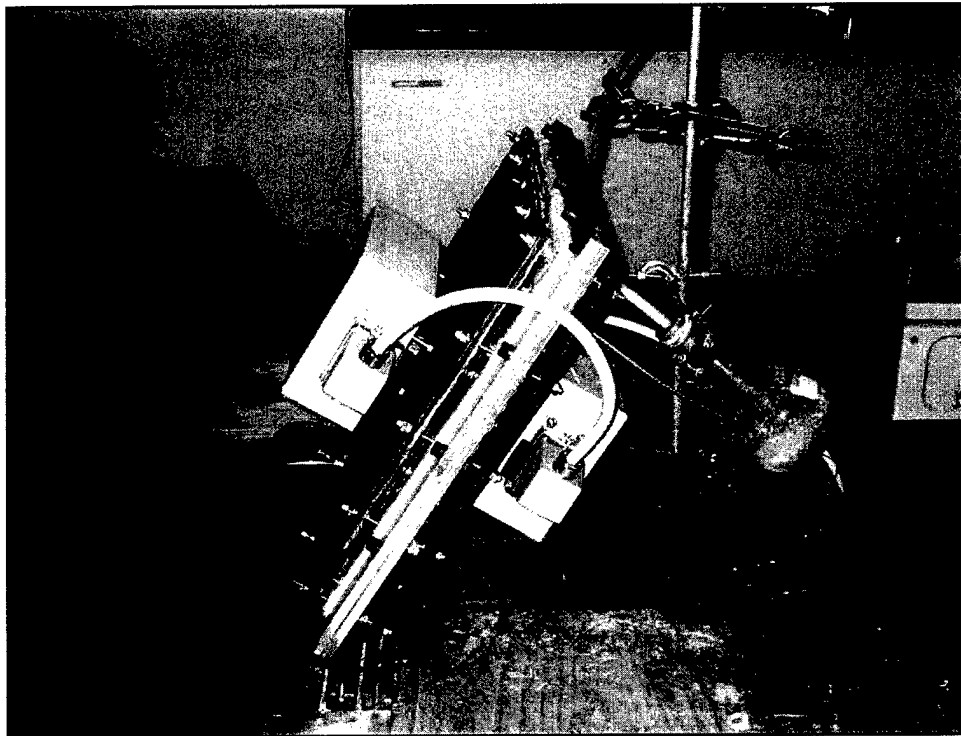


Figure 2. Heated Composite Tool (During Nitrogen Flush)

The cooling of the unit is by either natural convection or forced convection. As the cooling rate influences the degree of crystallinity of the Nylon copolymer both methods were tested. Forced convection cooling was powered by a standard 12 inch table fan. Natural convection cooling was achieved by merely switching off the heaters after the polymerisation phase and allowing the heat to dissipate.

#### 4.3 Hydraulic Composite Press

An industrial sized heated hydraulic press was utilised to create several composite plates. This tool was employed so that the effect of pressure on plate quality could be studied. Also, in order to produce tensile specimens, a much larger platen area was needed. The useable area of the press is 500mm x 500mm.

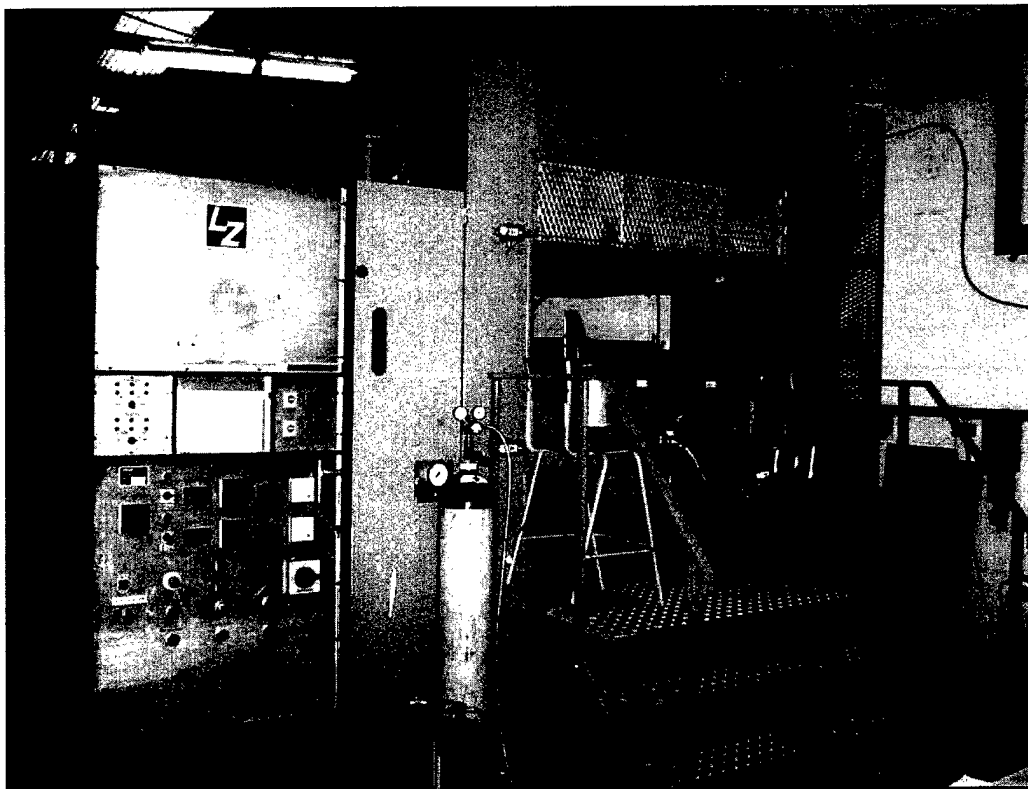


Figure 3 Hydraulic Press

Due to the high mass of the tool and the press heating mechanism a very large heat sink is created. Because of this massive heat sink the cool down rate for the parts is extremely low. Whilst the composite tool can be cooled down to a manageable temperature (approx. 40°C) in about an hour, it takes at least 12 hours to cool down the part to that same temperature with the hydraulic press.

## 5. Injection Process

The RTM process used in the fabrication of the plates in this project is a relatively simple one. Most of these trials were carried out by one person without any outside assistance. The basic procedure is as follows. It can be broken down into three main stages. These stages are the melting and mixing of the pre-polymers, the injection, and finally the polymerisation.

The melting and mixing stage is as follows. First of all the monomers are removed from their sealed bags and weighed according to the percentages required. If necessary they are dried under an inert atmosphere, a slight nitrogen overpressure is sufficient. Next the measured amount of monomers are placed consecutively into a flask and melted in the oil bath. The temperature of the oil bath must be above that of the highest monomer melting temperature. The melting temperature of caprolactam is 69°C and that of laurolactam is 151°C. A temperature of 175°C was chosen.

During the melting process nitrogen is fed into the flask to create an inert atmosphere. The mold is heated during this time to a temperature approximately the same as that of the melt. It is flushed for at least 15 minutes prior to injection in order to remove any moisture on the surface of the mold or the carbon fibers. After the caprolactam / laurolactam mixture has been thoroughly melted and mixed the injection portion of the process is ready to begin. The injection portion of the process starts by measuring an appropriate amount of the activator and catalyst solution, Grinolit. This is done using a pipette. The entire mixture is stirred for approximately 30-60 seconds depending on the volume of the melt. The vacuum is turned on and the inlet pipe is inserted into the flask. As the melt is being "sucked" into the mold the pressure must



be monitored carefully. If the vacuum is too strong the flow of the melt could become turbulent creating bubbles within the mold. If the vacuum is too weak there will not be sufficient force to push the melt into the mold. When enough of the mixture has flowed through the fiber bed into the outlet trap, the inlet and outlet are closed.

Once the entire mold has been sealed, the temperature of the mold is raised to the polymerisation temperature. The polymerisation time is a function of temperature. For these trials 20 minutes at 200°C was normally used. After this time, the mold is cooled below the melt temperature and the part can be removed.

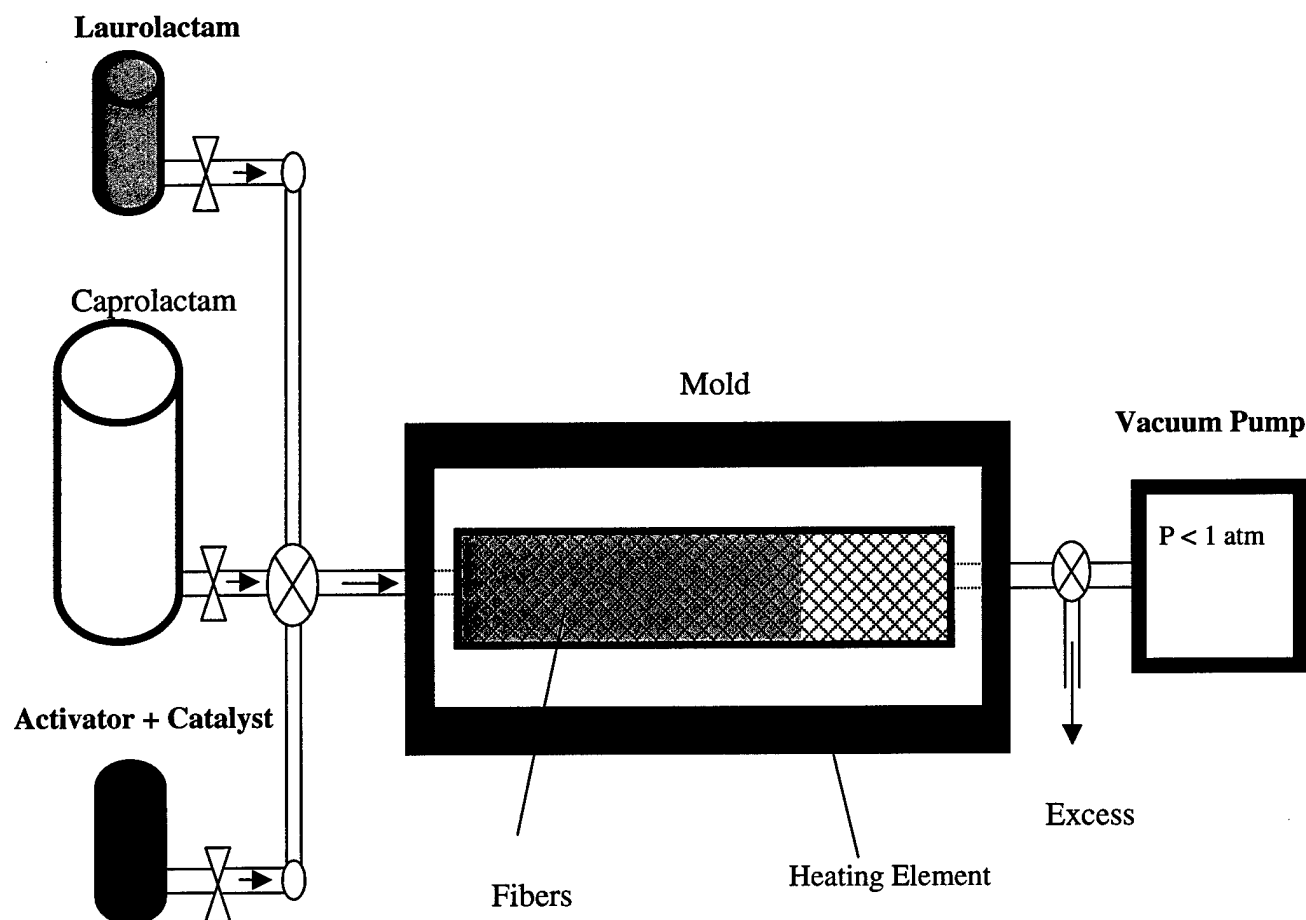


Figure 4. APLC 6/12 VARTM Schematic

The melting temperature of the copolymer depends on the polymer ratio and varies between the melt temperatures of PA 12 (178°C) and PA 6 (220°C). Because the predominantly PA 6 mixtures have a melt temperature above the polymerisation temperature the entire process can be considered isothermal. In industrial terms this means that a mold need not have a temperature cycle. That is to say that the fabrication process can have  $T_{\text{injection}} = T_{\text{polymerisation}} = T_{\text{demolding}}$ .

This is highly advantageous in the mass production of parts as the cycle time is not dependent on the mold heat up or cool down rate. However since the crystallinity of the polymer matrix depends on the cool down rate, in certain situations it may be necessary to cool down the part before demolding. If higher crystallinity is desired the part must be cooled down at a lesser rate. And vice versa.

## 6. Overcoming Voids in Processing

Thermoplastic composites in general have the draw back of low compression strength. Compression strength is greatly dependant on the properties of the matrix. In fact the compression strength of a polymer-matrix composite can often be lower than that of the matrix itself. This because the fibers themselves act as voids in the continuity of the polymer matrix thereby decreasing the compression strength. If you take this effect and add to it further voids, the drop in compression properties can be dramatic. It is for this reason that voids were of particular concern for this project.

In RTM voids can occur for a variety of reasons. These reasons include:

1. Variations in permeability on a filament and filament bundle scale
2. Outgassing of dissolved gas in the resin
3. Evaporation of volatile components in the resin
4. Shrinkage of the resin
5. Leakage in connections and mold. [3]

Four polymers were investigated during this project, PA 12, PA 6, 90/10 PA 6/12, and 95/5 PA6/12. The un-reinforced plaques fabricated in the laboratories were all perfect to the naked eye. Because of this it was determined that outgassing of dissolved gas in the resin and evaporation of volatile components in the resin were not problems associated with the processing of these polymers.

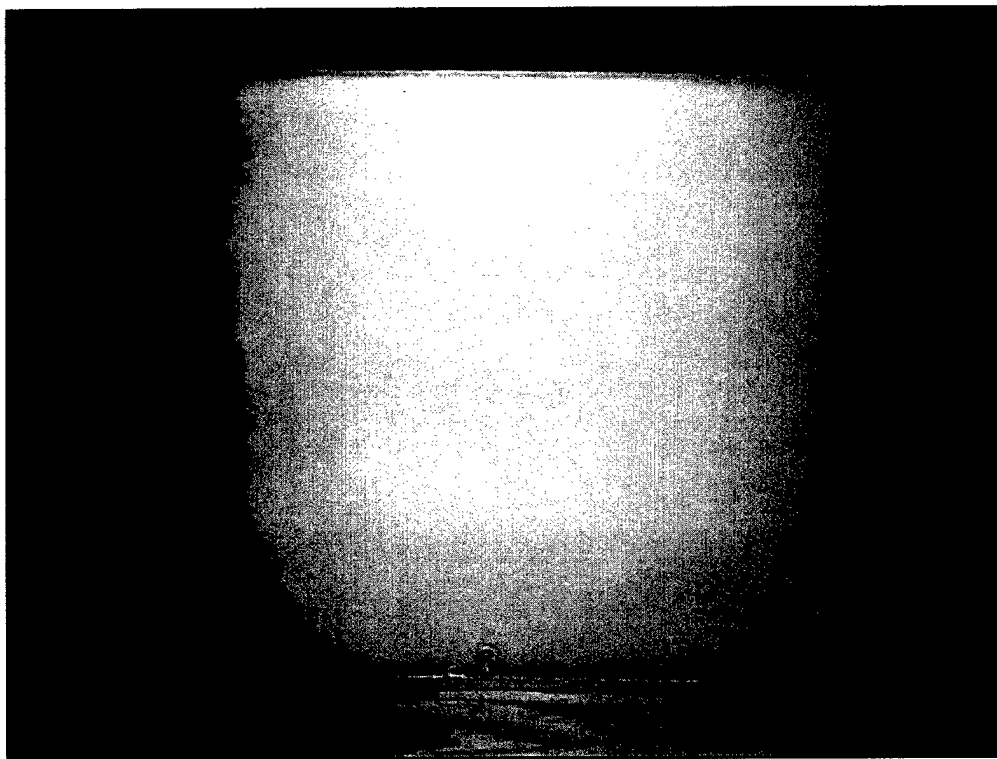


Figure 5. Polyamide 12 Plaque

However when the reinforced trials began it became obvious that void content could be a major problem. Many of the carbon fiber reinforced plates made were found to have a significant number of voids. These voids were clearly visible with the naked eye and were approximately 0.5 to 2 mm<sup>2</sup> in area. Upon further examination, voids were also found not only on the surface, but also throughout the laminate.

It was determined that these voids were formed due to shrinkage of the melt during its solidification process. In this case the polymer melt is constrained by the fibers and thus is not free to shrink. It was found that in woven fabrics, such as the ones used in this experiment, voids are often found at the intersection of the warp and weft directions. This is because the intersection points act as localised constraints on the melt, creating a discontinuous structure as it cools.

The number of voids was not consistent between the differing polymers and copolymers however. Because of the different shrinkages associated with the different polymers the appearance of the plates was different. PA 6 showed the highest shrinkage. By adding laurolactam to the melt you generally decrease the shrinkage value. The result of this is that the carbon fiber reinforced plates using PA 6 as a matrix show significantly more voids than the ones with a lesser PA 6 percentage. In fact the PA 12 plates manufactured under pressure show virtually no voids, with surface pitting at the fiber intersections being the only evidence of shrinkage.

In order to overcome the problem of voids created due to shrinkage a novel mold design was created. It was determined that to compensate for the shrinkage of the melt, the mold itself must be flexible. Therefore a relatively new injection process called Injection Compression Molding (I/CM) was employed.

The I/CM process is a combination of two commonly accepted methods of composite manufacturing, Resin Transfer Molding and Resin Film Infusion. Resin Film Infusion (RFI) involves the infusion of the resin into a dry fiber bed using pressure. The matrix is a solid before processing begins either in a film form or in pellet form. The reinforcement is arranged in layers with the matrix material sandwiched between the layers. When the entire sandwich structure is heated up the matrix melts and begins to flow in between the reinforcement. The application of pressure forces the remaining molten matrix into the fiber bed. After this the structure is cooled thus and the matrix to solidifies around the reinforcement.

I/CM as used in the manufacture of APLC 6/12 composites is carried out as follows. The reinforcement is laid up in the mold cavity (picture frame) as usual. As with the all the previous tests 4 layers of  $440 \text{ g/m}^2$  carbon fiber fabric were used. Next a

flexible polymer seal is placed around the perimeter of the mold. This seal is made from a material capable of withstanding the temperature and pressures of the molding process and it must be easily compressible. This project used a Silicon seal. The picture frame in this case is 2mm thick; the seal is also 2 mm thick. This essentially creates a 4mm thick cavity with 2mm being flexible and 2mm being essentially rigid. With this larger mold cavity the resin is injected using VARTM.

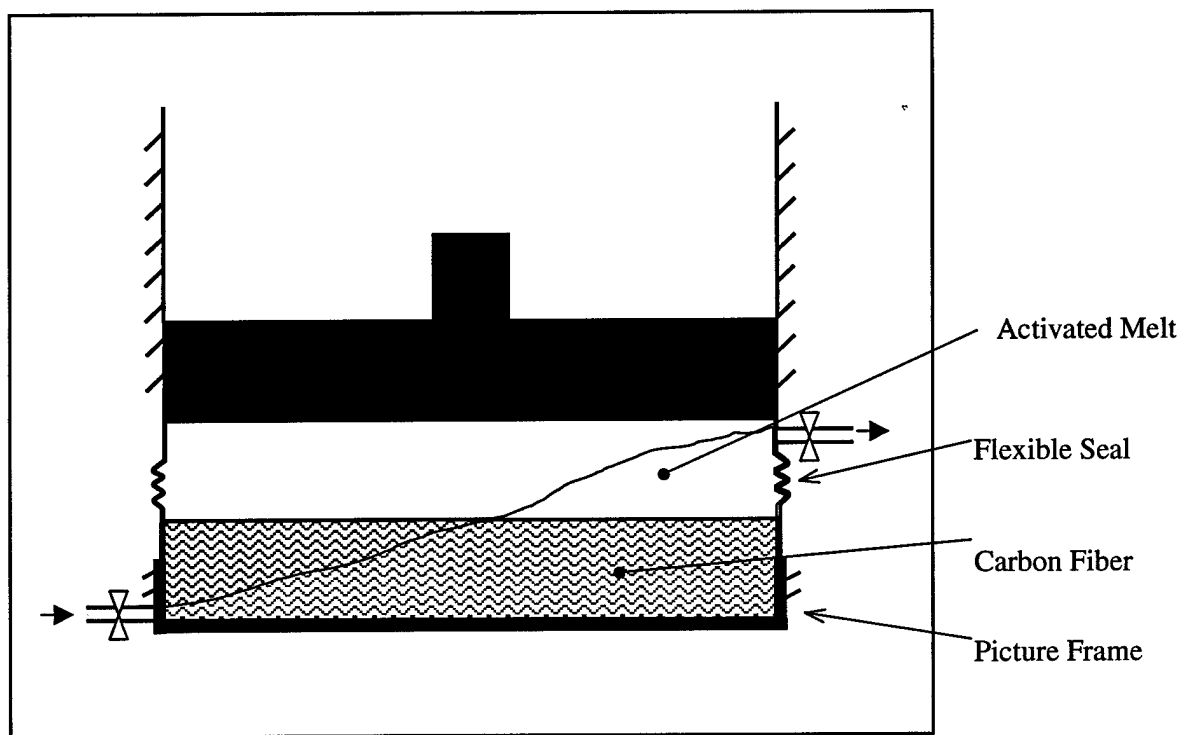


Figure 6. Mold Schematic During Modified VARTM Process

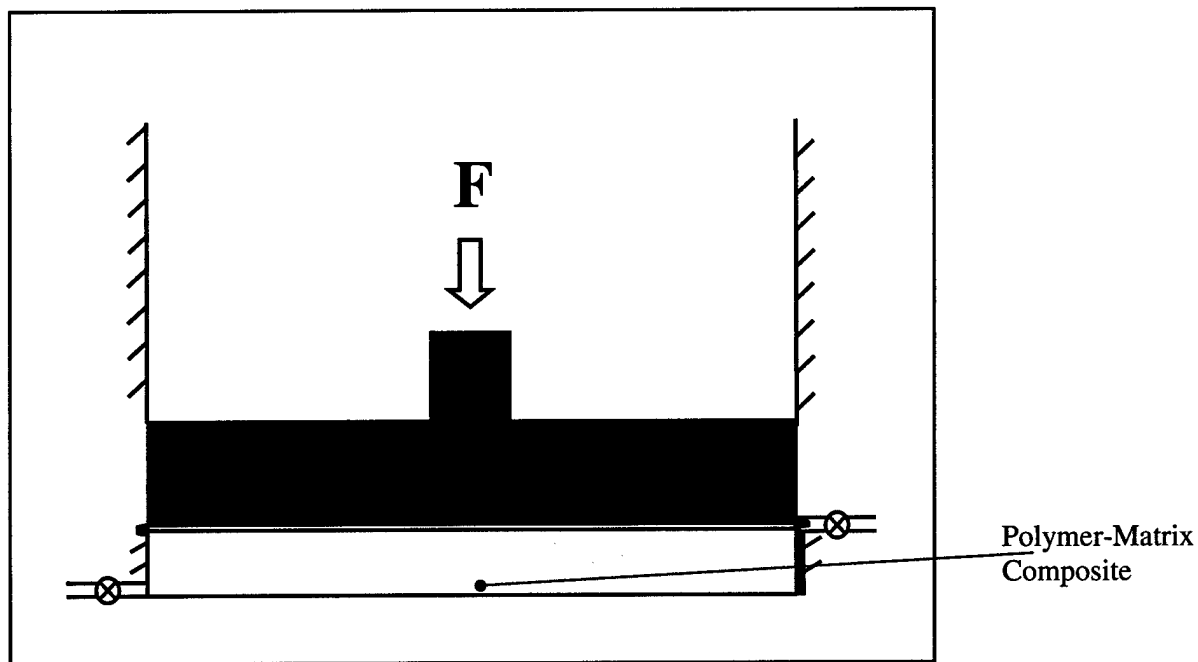


Figure 7. Mold Schematic During Polymerisation

Due to the large mold cavity there is a large difference in permeability along the fabric. In fact due to race-tracking much of the melt will flow over the surface of the fiber bed. The melt therefore will probably not have impregnated the fiber bed consistently. In order to force the resin into the fiber bed, pressure is applied immediately after injection. This pressure is maintained during the polymerisation process. As the viscosity of the melt increases the pressure is also increased. This creates a high level of compaction in the polymer-matrix composite. An increase in compaction will result in lower shrinkage. Because of this fact it is normally not necessary to increase pressure during the cooling process. Furthermore by keeping pressure on the mold during the entire cooling process you greatly increase the cycle time, thus increasing costs. The trials have shown that there is nothing to be gained by

doing so. The mere fact that more material has been forced into the fiber bed will greatly reduce the overall shrinkage of the matrix.

The results of this void free processing experiment have been somewhat promising. A 95/5 PA6/12 carbon fiber plate was fabricated using this process. Previously this material had very large problem associated with it due to a high void content. Using injection compression molding the void content has been reduced to virtually nil.



Figure 8. 95/5 PA 6/12 Carbon Fiber Plate Fabricated Using RTM Only



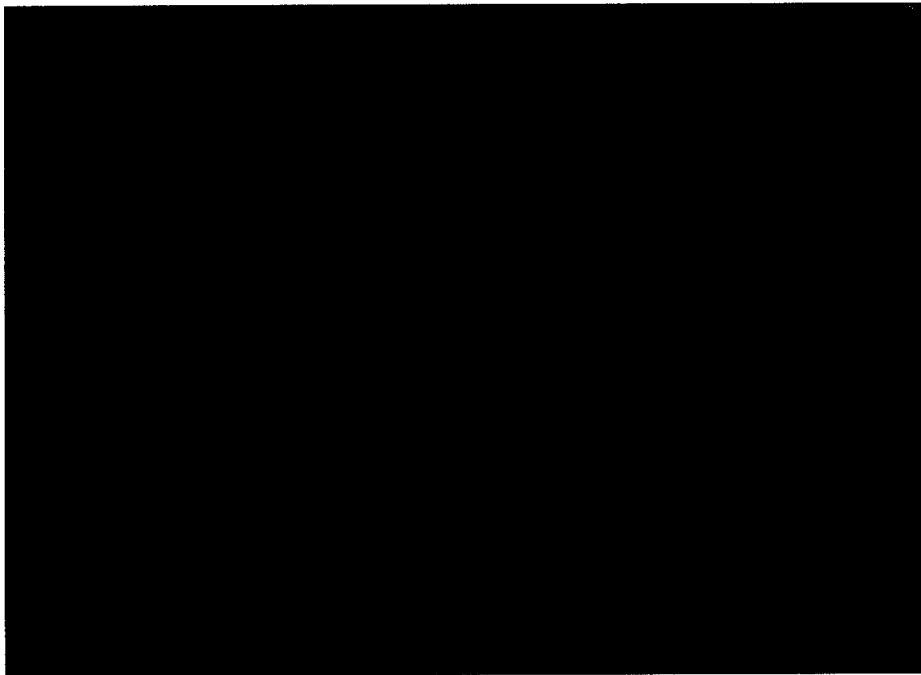


Figure 9. 95/5 PA 6/12 Carbon Fiber Plate Fabricated Using I/CM

The benefits gained from using this process were increased mechanical properties due to the lesser void content. All of this was achieved without any significant change in cycle time (compared to RTM). However, several additional problems were discovered. These include the usage of more matrix material, the fact that the process is only applicable for relatively simple shapes, and finally the problem of fiber wash.

Fiber wash is a phenomenon associated with fluid flow (the melt) over the reinforcement. As a viscous melt flows over the reinforcement its shear force causes the fibers to move. This effect can be quite significant and can lead to a large drop in mechanical properties.

**Fibers Have  
Moved**

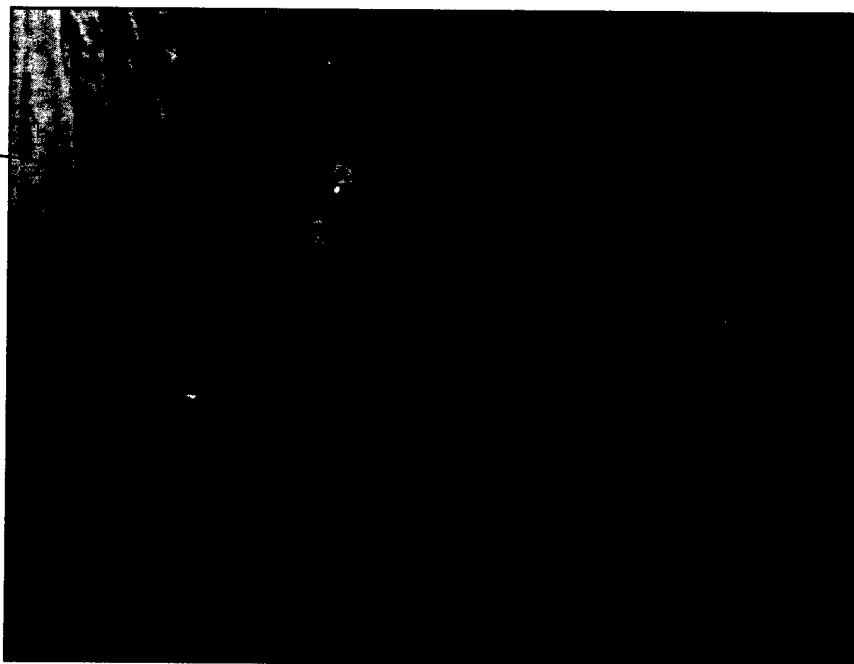


Figure 10. Fiber Washing Effect on 95/5 PA 6/12 Plate

## **7. Mechanical Testing**

For the mechanical testing no special preparations techniques were employed. All of the tests were performed at environmental equilibrium consistent with the ambient conditions. The fabricated plates were not stored in any special manner and therefore were allowed to normalise with the atmospheric conditions. The specimens were exposed to these conditions for a period of at least one month before testing. Given the climate in Galway, and therefore in the lab, the relative humidity of the air can be averaged at 50%. The temperature can be taken as a relatively stable 19°C. All of the tests were carried out according to the ASTM standards.

The mechanical tests for this project were carried out at three facilities, the Heavy Machines Laboratory, Mechanical Engineering department, the Biomedical Centre for Research, both part of the National University of Ireland, Galway, and Composites Testing Laboratory LTD. (CTL) an accredited private testing facility.

Computers connected to the testing machine recorded all of the testing results electronically using software supplied by the manufacturer of the testing machine. The exception to this being the Izod Impact Tester where the dial scale was read manually.

### **7.1 Un-Reinforced Testing**

#### **7.1.1 Tensile Testing**

The un-reinforced tensile tests were performed according to ASTM 638-00. All of the testing was performed in the Heavy Machines Laboratory located at NUI, Galway.

Material	E (MPa)	% Std. Dev.
PA 12	1296.4	2.1
90/10 PA 6/12	1222.8	7.1
95/5 PA 6/12	1789.8	6.1
PA 6	3046.8	4.0

Table 3. Tensile Modulus of Elasticity

Material	Max Stress (MPa)	% Std. Dev.
PA 12	45.4	8.4
90/10 PA 6/12	59.6	5.4
95/5 PA 6/12	60.8	11.0
PA 6	76.2	3.1

Table 4. Tensile Strength

Material	Max Strain (%)	% Std. Dev.
PA 12	402.8	9.7
90/10 PA 6/12	391.5	7.4
95/5 PA 6/12	387.4	7.6
PA 6	24.7	1.6

Table 5. Tensile Strain at Break

Material	$Y_{\text{stress}}$ (MPa)	% Std. Dev.
PA 12	33.04	6.0
90/10 PA 6/12	26.22	2.7
95/5 PA 6/12	35.80	2.8
PA 6	63.49	3.5

Table 6. Tensile Yield Strength

The results of the tensile tests were consistent with the expected results. The trend shows that 100% polyamide 6 had the highest tensile strength. Adding 5% polyamide 12 to the melt decreased the tensile strength by 20%. Adding another 5% only decreased it by a further 2%. 100% Polyamide 12 had the lowest tensile strength, which is in line with literature. In terms of polymer-matrix composites the tensile strength of the matrix did not have a large affect on the overall tensile strength of the composite. Nearly all of carbon fiber composite's tensile strengths lies with the carbon fibers.

Similar trends existed for the tensile modulus results. Polyamide 6 had the highest value at 3 GPa. Adding 5% PA 12 decreased the stiffness of the copolymer significantly (41% less). As with the literature, when the amount of mixing increased the stiffness decreased. This is again due to the percentage crystallinity that decreases with the amount of mixing. For this reason the 90/10 PA 6/12 had the lowest stiffness at 1.22 GPa. Increasing the mixture to 50/50 would lower the stiffness to its lowest level.

The yield strength of the copolymer follows a similar trend to the modulus. Again Polyamide 6 has the highest yield strength. As polyamide 12 is added to the polyamide 6 the strength of the copolymer decreases. However 100% polyamide 12 has a higher yield strength than the 90/10 copolymer mix. This to be expected as the crystallinity of the copolymer should decrease with the more mixing. Greater crystallinity generally means higher tensile and yield strengths.

A very interesting result lies in the elongation at break results. Polyamide 6 breaks at about 25% strain. By adding some PA 12 to the mixture one would expect the percentage elongation to increase somewhat. However, by adding 5% PA 12 to the mix the elongation increases by an astonishing 1468%. By adding a further 5% PA 12 to the copolymer the elongation increases by a mere 1%. And 100% PA 12 has an elongation which is 4% greater than that of the 90/10 PA/12 mix. The 95/5 PA 6/12, the 90/10 PA 6/12 and the 100% PA 12 all have similar elongations with only 4% difference between them.

### 7.1.2 Flexural Testing

Material	E (MPa)	% Std. Dev.
PA 12	733.9	5.7
90/10 PA 6/12	851.8	8.3
95/5 PA 6/12	1476.3	6.3
PA 6	1319.0	2.2

Table 7. Flexural Modulus of Elasticity

Material	Yield Stress (MPa)	% Std. Dev.
PA 12	40.55	10.0
90/10 PA 6/12	45.33	4.4
95/5 PA 6/12	75.43	4.6
PA 6	72.37	5.3

Table 8. Flexural Yield Strength

Normally nylon does not fail in flexure tests as it does not fail until it has reached a large displacement. Because of this these large displacements the specimen will slip between the supports. Due to the large span and small cross sectional area, the maximum stress could not be reached. For these tests only the Young's Modulus and Yield Stress were reported. The flexure tests were performed at NUI, Galway according to ASTM 790-00.

### 7.1.3 Notched Izod Impact Testing

The Impact tests were performed according to ASTM D 256-00

Material	I.S (J/m2)	% Std. Dev.
PA 12	10.0	0.2
90/10 PA 6/12	4.4	3.6
95/5 PA 6/12	2.3	11.7
PA 6	3.6	10.5

Table 9. Notched Izod Impact Strength

The results of the Notched Izod impact tests were somewhat surprising. Polyamide 12 had by far the highest impact strength, as expected. The Polyamide 6 results are higher than expected. In keeping with the literature 90/10 PA 6/12 had a strength in between that of the two polymers, however; unusually 95/5 PA 6/12 did not.

By adding 5% laurolactam to the melt the impact strength actually decreases by 36%. However adding a further 5% laurolactam to the melt increases the strength by 91%. The surprising results are more than likely due to differences in crystallinity and moisture absorption. Increasing crystallinity decreases impact strengths. Furthermore PA 6 absorbs water readily, which acts as a plasticizer thus increasing impact strengths. Therefore the anomalous results are more than likely due to a combination of these two factors.

## 7.2 Reinforced Testing

### 7.2.1 Tensile Testing

Material	E (MPa)	% Std. Dev.
PA 12	21.25	5.3
90/10 PA 6/12	21.33	3.9
95/5 PA 6/12	21.78	2.2
PA 6	20.86	4.0

Table 10. Tensile Modulus of Elasticity



Material	Max Stress (MPa)	% Std. Dev.
PA 12	523.2	9.5
90/10 PA 6/12	533.0	10.1
95/5 PA 6/12	506.6	5.7
PA 6	494.9	11.1

Table 11. Tensile Strength

The tensile and flexure tests were carried out in the heavy machine laboratory of NUI, Galway according to ASTM D 3039/D 3039M-00. A Zwick Universal testing machine performed the tests. In order for the tests to be significant the failure should occur between the end tabs, i.e. in the gauge length. During these tests most of the failures occurred within, or in close proximity to, the gauge length.

Polymer matrix composites in tensile are dominated by the properties of the fibers. The matrix therefore does not have a significant effect on the tensile strength of the composite under normal conditions. It can be seen from these results that there is no significant difference in either the tensile modulus or the tensile strength of the specimens.

## 7.2.2 Flexure Testing

Material	E (MPa)	% Std. Dev.
PA 12	34.93	2.2
90/10 PA 6/12	11.70	21.4
95/5 PA 6/12	26.02	12.2
PA 6	33.10	5.3

Table 12. Flexural Modulus of Elasticity

Material	Strength (MPa)	% Std. Dev.
PA 12	770.2	3.6
90/10 PA 6/12	605.9	6.4
95/5 PA 6/12	713.9	4.9
PA 6	812.2	4.6

Table 13. Flexural Strength

All of the specimens failed at relatively low strains. Nearly all of the specimens failed due to buckling of the fibers on the upper surface of the sample. A few of the specimens had a multimode failure exhibiting buckling on the top of the sample and also some tensile fracturing on the bottom of the sample. This was found to be in only a few cases with individual fibers being broken.

It can be seen that the polyamide 6 reinforced composites have the highest flexural strength. Polyamide 12 has the second highest flexural strength with the copolymer-reinforced samples having the lowest strengths. The yield strength of the materials

follows a similar pattern the exception that the polyamide 12 has a slightly higher strength than the polyamide 6.

It should be noted at this point that many of the samples contained a significant number of voids. The polyamide 12 laminates had the lowest void content, the void content increased with the amount of caprolactam added to the melt. The result being that the polycaprolactam (PA 6) plate had the most voids. While void content is not a significant problem in fiber dominated tests such as tensile, in compression testing the matrix properties are more important. As flexural loading is a combination of compression and tension both the matrix and fibers are critical. Therefore void content was very important as can be evidenced by the failure in buckling.

The flexural modulus of elasticity had a similar trend to the maximum strength and yield strength. Polyamide 6 and polyamide 12 had the highest moduli. The copolymer reinforced composites had lesser moduli as expected due to the decrease in crystallinity. By adding 5% laurolactam to the melt, the balance being caprolactam, the modulus of elasticity was reduced by 21%. Adding an additional 5% laurolactam decrease the modulus a further 55%. This means that by adding a mere 10% of PA 12 to the PA 6 melt decreases the modulus by an astonishing 65%.

### 7.2.3 Compression Testing

An evaluation of a thermoplastic composite would not be complete without performing a compression test. Traditionally thermoplastic materials do not perform well in compression as compared with thermosets. This is due to the fact that thermoplastics have long chain molecules that can slip past one another when stressed. While this increases impact strengths, it does have a negative effect on compression strengths. Thermosets have cross-linking molecules that do not easily

slip and thus form a semi-rigid structure. For this reason thermosets generally have much higher compression strengths.

The tests performed were Celanese Compression according to specification EN 2850. The machining, specimen preparation, and testing were carried out at Composites Testing Laboratory LTD. Materials supplied were in the form of laminates that had been manufactured in the labs of NUI Galway.

The testing machine was a Zwick testing machine, model 148670. The specimens were gripped using flat-faced hydraulic grips and were loaded at 1 mm/min until failure. The specimens were mounted in a purpose built Celanese compression fixture. A DSST Biaxial Extensometer measured the strain of the specimens. Computer software designed by Zwick produced Force vs. Displacement graphs, and calculated the compression strength and Young's modulus.

Material	E (MPa)	% Std. Dev.
PA 12	37.71	7.7
90/10 PA 6/12	40.53	10.8
95/5 PA 6/12	39.25	10.1
PA 6	43.07	6.4

Table 15. Compression Modulus of Elasticity

Material	Strength (MPa)	Std. Dev.
PA 12	175.5	6.7
90/10 PA 6/12	183.6	6.0
95/5 PA 6/12	144.5	6.9
PA 6	206.6	5.8

Table 16. Compression Strength

The results of the compression tests were slightly lower than the expected results. The trend shows that polyamide 6 had the highest tensile strength. Adding 5% polyamide 12 to the melt decreased the tensile strength by 30%. Adding another 5% actually increased the strength by 27%. Polyamide 12 had a relatively high compression strength compared to that of the copolymers at 175.5 MPa. It had been assumed that PA 12 would have the lowest strength. This however, is not the case.

The results of these tests cannot be considered to be very accurate due to the presence of voids. As stated before, the presence of voids greatly influences the compression strength of composite materials. If the voids were to be reduced or eliminated, the expected results would be significantly higher.

#### 7.2.4 I/CM Void Free Plate

The plate fabricated using the I/CM method contained 4 layers of carbon-fiber fabric. This was the same lay-up as the other reinforced plates. However, the addition of the flexible seal caused the thickness of the finished polymer-matrix composite to increase. This increase in thickness (from 2mm to 3.5mm) caused a reduction in the fiber volume fraction. The I/CM plate had a volume fraction of 29%.

With regards to mechanical testing, it is not very practical to compare fiber-reinforced composites with different fiber volume fractions. Therefore in order to compare this plate with previously manufactured plates (50% fiber-volume fraction) the results were adjusted. By assuming that the I/CM plate had the same thickness as the other plates (2mm), we can effectively increase the fiber-volume fraction from 29% to 50%. The compression strength and modulus were calculated using this theoretical thickness.

Material	E (GPa)	% Std. Dev.
95/5 PA 6/12	38.80	12.4

Table 17. Compression Modulus of Elasticity(50% Volume Fraction)

Material	Max Stress (MPa)	% Std. Dev.
95/5 PA 6/12	211.8	7.0

Table 18. Compression Strength (50% Volume Fraction)

Using I/CM the compression strength of the 95/5 PA6/12 carbon-fiber reinforced material is 211.8 MPa.

This represents a 43% increase in strength when compared with a 95/5 PA6/12 carbon-fiber reinforced fabricated by RTM only. With respect to stiffness, the material's compression modulus increases to 38.80 GPa. This also represents a 43% increase. Obviously this is a significant increase in material properties hence the

modified injection process shows its great potential.

#### 7.2.5 Compression After Impact Testing

Material	Compression Strength (MPa)	Std. Dev
PA 12/CF	100.25	4.31
PA 6/CF	125.20	1.56

Table 19. Compression After Impact Strength

The test performed was Compression After Impact tests according to specification AITM 1.0010. The machining, specimen preparation, and testing were carried out at the Composites Testing Laboratory, Galway. Materials supplied were in the form of laminates that had been manufactured in the labs of NUI Galway.

The test consists of two parts, impact and compression. The impact portion of the test was carried out at the Biomedical Research Centre at NUI, Galway by CTL personnel. Specimens are mounted in a Rosand drop weight impact tester and then impacted with energy equivalent to 20 Joules. The specimens were then taken to CTL for the compression portion of the test. The specimens were mounted in a purpose built Boeing compression after impact fixture from Wyoming Test Fixtures. A DSST Biaxial Extensometer measured the strain of the specimens. Computer software designed by Zwick produced Force vs. Displacement graphs, and calculated the compression strength and Young's modulus.

### 7.2.6 Moisture Absorption

Tests for moisture absorption were carried out according the ASTM Designation: D 570-98. The test's function is to determine the percentage increase in a material's weight due to moisture absorption under certain conditions. Three different tests were employed.

Firstly the equilibrium absorption content of each sample was determined. This was done by exposing the samples to standard atmospheric conditions for an extended period of time (1500+ hours). In order to calculate the amount of water absorbed during this time the samples were first weighed, then dried for 24 hours at 50 °C and re-weighed. The difference between the conditioned and the dry weights was determined for each sample tested. These results were then averaged and converted to a percent increase in weight.

Secondly the amount of moisture absorption due to the immersion of the material in distilled water for 24 hours at 23°C was determined. After the exposure time the samples were removed, towel dried (to remove surface water), and re-weighed. Percentage increase was calculated using the same method as above.

Thirdly the amount of moisture absorption due to the immersion of the material in distilled water for 2 hours at 100°C was determined. After exposure the samples were cooled in distilled water at 23°C for 10 minutes, towel dried, and weighed. The percentage weight increase was again calculated as above.



Material	% Weight Increase	% Std. Dev.
PA 12	0.30	3.3
90/10 PA6/12	0.61	6.5
95/5 PA6/12	0.56	3.6
PA 6	0.53	7.5

Table 20. Moisture Absorption Due to Long Term Environmental Exposure  
(50% Relative Humidity @ 23 °C)

Material	% Weight Increase	% Std. Dev.
PA 12	0.17	5.9
90/10 PA6/12	1.02	6.9
95/5 PA6/12	0.88	2.3
PA 6	0.68	4.4

Table 21. Moisture Absorption due to 24 Hour Immersion @ 23 °C

Material	% Weight Increase	% Std. Dev.
PA 12	0.65	3.1
90/10 PA6/12	3.14	3.5
95/5 PA6/12	2.76	2.9
PA 6	2.06	5.8

Table 22. Moisture Absorption due to 2 Hour Immersion @ 100 °C

### 7.2.7 Effect of Polymerisation Temperature on Moisture Testing

Material	%Weight Gain	Std. Dev.
PA6 (210C)	0.95	5.3
PA6 (200C)	1.29	5.4
90/10 PA6/12	0.97	6.2
PA 12	0.13	7.7

Table 23. Moisture Absorption due to 24 Hour Immersion @ 23 °C

Material	% Weight Gain	Std. Dev.
PA6 (210C)	1.68	5.9
PA6 (200C)	2.23	4.5
90/10 PA6/12	2.24	5.3
PA 12	0.59	6.8

Table 24. Moisture Absorption due to 2 Hour Immersion @ 100 °C

To study the difference between the effects of processing temperatures on moisture absorption properties two polyamide 6 plates were fabricated. Both plates were manufactured using identical processing techniques with the only difference being the temperature of polymerisation. One was created using the recommended polymerisation temperature of 200 °C, the other plaque used 210 °C. Two percent activator and catalyst solution was employed in all cases.

It was thought that the PA 6 plate processed at a higher temperature would have lower moisture absorption characteristics. By processing a plaque at 210 °C the crystallinity of the material should be greater than that of a plaque processed at 200 °C. This is due to the fact that it takes longer to cool down from the elevated temperature thus giving the long chained molecules more time to arrange themselves in an orderly fashion. Higher crystallinity should lower the moisture absorption of the material.

A Polyamide 12 and a 90/10 Polyamide 6/12 plaque was also processed. These two additional plates were processed at the recommended temperature of 200 °C. All other processing conditions were identical to that of the polyamide 6 plaques. The plaques were used to compare relative moisture absorption properties.

When we compare the results for polyamide 6 we see that the processing temperature does affect the moisture absorption properties. As predicted the PA 6 plaque processed at the higher temperature (210 °C) has a lower moisture absorption for the various tests. In fact it can be seen that by increasing the polymerisation temperature by only 10 °C we can reduce the “24 Hour Immersion” absorption by 26%. Furthermore the “2 Hour Boiling Test” shows a 25% decrease in the moisture absorption.

It is assumed that this reduction in the level of moisture absorption during these tests is due to the increase in the crystallinity of the material. Greater crystallinity means lesser moisture absorption. Therefore it can be determined that any method used during the fabrication process to increase crystallinity will lower the moisture absorption. From literature we have seen that higher processing temperatures increase the percentage crystallinity of the molded material. [1] This is evidenced in the testing by the lower moisture absorption.

The addition of laurolactam into the melt generally reduces the moisture absorption properties of the polycaprolactam. [5] Surprisingly this was found not to be the case in several of trials and contradicts many different literature sources. While the copolymer mixtures did exhibit low absorption rates compared with published PA 6 data, when compared with the PA 6 tested in this project it did not represent any significant improvement.

This could be due to several factors-

- The PA 6 samples represented very crystalline polymers and therefore did not absorb much water
- The PA 6 contained very low residual monomer content and therefore did not absorb much water.
- The copolymers tested had high residual monomer content, thus increasing absorption.
- Combinations of the above.

Comparing the materials processed at 200°C in the 24-hour immersion test, the PA 6 has highest absorption at 1.29 wt.% gain. Adding 10% laurolactam to the melt produces a 25% decrease in absorption. The polyamide 12 material had the lowest values at 0.13 wt.% gain.

Comparing the materials processed at 200°C in the 2-hour boiling immersion test, the PA 6 has highest absorption at 2.23 wt.% gain. Adding 10% laurolactam to the melt does not change the absorption during this test. This was an interesting and unexpected result.

It is likely that some residual monomers were dissolved at the higher testing temperature and was replaced by water. The polyamide 12 material had the lowest values at 0.13 wt.% gain.

Test	% Weight Increase
24 Hour Immersion	1.6
50% Relative Humidity Equilibrium	2.7
Saturation	9.5

Table 25. Moisture Properties of Hydrolytic PA 6 [1]

Test	% Weight Increase
24 Hour Immersion	N/A
50% Relative Humidity Equilibrium	0.8
Saturation	1.6

Table 26. Moisture Properties of Hydrolytic PA 12 [1]

### 7.2.8 Shrinkage

The shrinkage values were all calculated by measuring the difference between the width of the mold cavity and the width of the finished copolymer plate. This measurement is taken transverse to the flow direction. Because the mold is tilted at 60° gravity will spread the flow filling the width therefore the mold is assumed to be filled in this direction. It was not possible to measure the amount of shrinkage in line

with the flow as it did not always reach the outlet nozzle. Due to this unpredictability of the amount of mold filling in line with the flow, it is not possible to measure the shrinkage values in that direction.

Material	% Reduction (Transverse to flow)
PA 12	1.33
90/10 PA 6/12	0.67
95/5 PA 6/12	0.83
PA 6	2.17

Table 27. Shrinkage Values

Published data on shrinkage of anionically polymerised laurolactam and caprolactam reports that there is virtually no shrinkage of laurolactam, but 10-12% for caprolactam. Large shrinkage values can lead to various problems including the formation of voids, bubbles, and internal stresses. [6]

Material	Shrinkage
APLC 12	$\approx 1\%$
APLC 6	10-12%

Table 28. Typical Hydrolytically Polymerised Shrinkage Values

In the trials carried out at NUI, Galway the shrinkage of polyamide 6 was 2.3%, which is almost double that of polyamide 12. The value for polyamide 6 does represent a 77-80% reduction in shrinkage. The polyamide 12 value is 1.33%. This level of shrinkage has not been shown to cause any significant problems in the fabrication of RTM polymer composite.

Shrinkage is very important when it comes to advanced composites. If a matrix shrinks it cannot fully consolidate the fibers. The fibers act to constrain the matrix as it is cooling which leads to voids. Therefore the higher the shrinkage the higher the void content. This agrees with the visually perceived results concerning the void content. The plates with the highest void contents were those composed mainly of PA 6. However, the shrinkage values for the copolymer, 90/10 PA 6/12 and 95/5 PA 6/12, are surprisingly low at 0.67% and 0.83% respectively. This would suggest that RTM impregnated composites using these materials would have very few voids. This, however, does not agree very well with the perceived void content. Both of the copolymer plates exhibited large void contents in all trials.

## 8. Conclusions

The material investigated is an anionically polymerised lactam 6/12 carbon fiber reinforced composite. The means of processing was vacuum assisted resin transfer molding using a rigid mold. The material and the processing technique will be discussed separately.

Anionic polymerisation using the GRILONIT system proved to be a quick, clean, and reliable method of producing polyamide 6, polyamide 12, and polyamide 6/12. Both the polymers and copolymers exhibited good mechanical strengths as well as good toughness and abrasion resistance. APLC 6 generally exhibited the highest tensile and flexural properties. APLC 12 generally exhibited the highest impact strengths. All of the materials fabricated possess the traits of engineering thermoplastics.

The mechanical and physical properties of APLC 6/12 proved to be a compromise between APLC 6 and APLC 12. For the most part all of the properties of APLC 6/12 tested lay in between those of APLC 6 and APLC 12. Mechanical tests including, tensile tests, flexural tests, and notched Izod impact tests supported this statement.

In terms of physical testing, the melting temperature (evaluated by DSC) verified the compromise. Unusually the moisture absorption tests did not support this theory. Rather than being a compromise between the APLC 6 and APLC 12, the copolymer actually had a higher rate of moisture absorption in two of the tests. This was unexpected as it has been shown in literature and in practice that adding laurolactam to caprolactam will reduce the absorption rate. It was assumed that this anomaly was due to a combination of two factors, the difference in crystallinity and the difference in residual monomer content. However although the trend of reducing moisture content with increasing laurolactam content was not fulfilled, all of the moisture test



results proved to be very promising. Each of the tests showed a lower moisture content than in the literature. Because of this polyamides processed by anionic polymerisation seem to have a bright future.

Thermoplastic composite materials are the future of the composite industry. Their ability to be recycled and their improved toughness offers distinct advantages over their thermoset counterparts. Also, vastly reduced cycle times, ease of storage, and ease of handling, produce the potential for mass production.

Traditionally it has not been easy to mold thermoplastic-reinforced composites due to their high viscosities. High temperatures and pressures were always required to fully impregnate fiber beds. Liquid composite molding was virtually impossible. The employment of an activated monomer melt eliminates the problems associated with high viscosity. The composites fabricated in this thesis were impregnated using only a vacuum pump i.e. low pressure.

The cycle time on the plates manufactured was also low. The wetting of the fiber bed (injection time) was on the order of seconds. Polymerisation time, in this case, was 20 minutes. By increasing the polymerisation temperature by a few degrees it was found that both the mechanical and physical properties of the composite were improved.

It has been shown that the matrix fulfils the requirements for direct impregnation of reinforced-reinforced preforms. The matrix viscosity is very low. Once impregnated the melt can be solidified in a reasonable amount of time. The resultant matrix has high enough properties to give good mechanical and physical stability to the composite.

Applications of this polymer-matrix composite include automotive parts, sporting goods, and high production structural parts. These include structural parts of cars such as bumpers, hoods, as well as interior components.

Currently the problems with void content will not allow the material to be used in very high performance applications such as aeronautical and aerospace. However the problems of void content could be alleviated on an industrial level relatively easily. Injecting a small amount of melt into the already impregnated fiber bed immediately after the RTM would increase compaction. This additional step reduces the shrinkage, thus reducing (or eliminating) the voids.

Future work includes optimising the copolymer with respect to crystallinity and filler compounds eg. plasticizers, additives, colouring etc. In terms of engineering work, more research can be done on the reinforcement itself. For example glass fiber or aramid fiber could be investigated as a possible reinforcing material. Furthermore an industrial type production line could be set up to test the materials potential for mass production.

In conclusion the anionic polymerisation of polyamide copolymers as a matrix for advanced composites proved to be successful. The VARTM processing method proved to be a simple and effective way to impregnate the fiber bed. However this method did not produce the necessary compaction in order produce void free plates. By adding an additional injection step or by using injection compression molding the problem of voids can be overcome.

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